REPORT

FIRST RESEARCH COORDINATION MEETING OF THE IAEA COORDINATE RESEARCH PROJECT F22070 ON

“ENHANCING THE BENEFICIAL EFFECTS OF RADIATION PROCESSING IN NANOTECHNOLOGY”

18 – 22 MARCH 2019,
VIENNA, AUSTRIA
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FOREWORD

Radiation processing has long been recognized as an energy efficient technology with strong application potential in several industrial areas. Today, the specific advantages it presents are being utilized by nanomaterials and nanoscale engineering for applications in such diverse sectors as medicine and healthcare, electronics, energy, environment, advanced materials and food and agriculture. It is important that up-to-date information on nanoscience and nanotechnology be shared among academic and industrial research centers with complementary expertise. Sharing this information will support Member States in developing methodologies and technologies for the use of radiation in the synthesis, modification, fabrication, and characterization of nanomaterials.

The IAEA is the world's central intergovernmental forum for scientific and technical co-operation in the nuclear/radiation field through its technical cooperation programmes, coordinated research projects, consultants and technical meetings and conferences. IAEA conducted the Coordinated Research Project on ‘Nanoscale Radiation Engineering of Advanced Materials for Potential Biomedical Applications (2008-2012), ‘Radiation Curing of Nanocomposites for Enhancing their Features and Utility in Healthcare & Industry’ (2010-2014) and published their achievement as a technical report (IAEA RADIATION TECHNOLOGY REPORTS No. 5).

Based on the requests and information from the member states, IAEA organize the 'Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology' (F22070). The aim of this CRP is to develop radiation-driven nanofabrication process for value-added products and to provide structural and functional parameters for the nanofabrication. This CRP will attain the control of key parameters in radiation processing, such as radiation-induced chemical reactions, template effect on metal ions reduction, structural parameters such as size, shape and composition of nanomaterials, distribution of anchoring points and surface properties in radiation-grafted materials, and also address some specific issues mainly related to methodological and technological aspects, as well as include deeper exploitation of recent advances in swift heavy ions (SHI) irradiation and the emerging concept of nano-processing.

The first Research Coordination Meeting (RCM) was held in Vienna from 18 to 22 March 2019 at the IAEA to review the status of present understanding of the effect of ionizing radiation on nanoscale science and engineering, and revisit scientific breakthroughs on the new concepts that may invite development of the new generation of nanoengineering products. In the meeting, identification of emerging
needs and gap areas in the research and development for nanoscale science and engineering and cooperative
and networking activities among the participating laboratories were discussed.

This report of the meeting is divided into two main parts: the first part gives a summary of the talks
by the participants, as well as the identified needs and gaps that need to be addressed for potential use of
radiation technology for further researches in nanoscience/nanotechnology, followed by recommendations
to the IAEA. The second part of the report contains a more detailed contribution by the meeting participants.
1. INTRODUCTION

Radiation processing has been long recognized as an energy efficient technology with strong perspectives in several industrial areas. Nowadays, nanomaterials and nanoscale engineering exploiting the specific advantage of radiation processing start to be used not only in medicine and healthcare sector, but also for other challenging applications such as electronics, energy, environment, advanced materials, food and agriculture.

The present Coordinated Research Project (CRP) for “Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology” (F22070) has been initiated by IAEA for strengthening the capabilities of the Members States to:

- Deepen the current knowledge in the synthesis of nanomaterials using radiation processing
- Develop new materials and systems in the perspective of specific applications is one or several key domains (healthcare, food and agriculture, environment, electronics, packaging, cultural heritage preservation (coatings), structural materials (high performance composites, industrial coatings)
- Explore new possibilities for using radiation-processed nanomaterials in new application areas
- Initiate new scientific collaborations and to intensify the of existing networks
During the first two days of the meeting, the 21 participants originating from 19 countries have presented their background activities at national or laboratory level and developed the main objectives and the workplan of their research programme.

2. **CRP OVERALL OBJECTIVES**

   The primary goal of this CRP is to exploit innovative methodologies and technologies in order to fabricate high performance and high value-added nano-products for applications in electronics, energy, environment and advanced materials.

2.1. **SPECIFIC RESEARCH OBJECTIVES**

1. To develop processes, techniques and protocols for radiation-driven nanofabrication of value-added products;
2. To investigate key factors behind scientific challenges in radiation processing, such as structural and functional parameters, and methodological and technological aspects;
3. To endeavour to transfer research results to end-users;
4. To establish and develop the network of collaboration in the field of radiation-driven nanofabrication.
2.2. OVERAL EXPECTED OUTCOMES & OUTPUTS

Through the CRP, enhanced capability of member states in application of nanotechnology to environmental protection and remediation, electronics and energy, and advanced functional materials will be expected.

- Novel value-added products based on nanomaterials for industrial applications;
- Simulation techniques for design of new nanomaterials;
- Protocols for synthesizing and testing of selected nano-materials by radiation processing;
- Network of researchers in nano-fabrication using radiation

3. CURRENT STATUS OF R&D WORK IN INDIVIDUAL INSTITUTIONS AND WORK PLAN

3.1. PARTICIPATING MEMBER STATES

Brazil, Egypt, France, Indonesia, Italy, Japan, Kazakhstan, Malaysia, Morocco, Philippines, Poland, Portugal, Republic of Korea, Russian Federation, Serbia, Thailand, Turkey, United Kingdom, Viet Nam

BRAZIL

Metal and metal oxide/Graphene-based nanocomposites have attracted attention due to their peculiarities in combining properties for many applications, such as for energy storage, electrochemical devices, fuel cell technology, catalysis, sensing and photonics.

Chemical method for the incorporation of metal nanoparticle on graphene based nanomaterials involves toxic reagents, such as NaBH₄, amines and hydrazine. For non-toxic reducers such as glucose, the reaction time ranges from 30 minutes to 2 hours. In addition, trace amount of these highly toxic reagents remains on the sheet surface after reduction process, decreasing the performance of the nanocomposites. Our research group has already obtained metal/graphene-
based nanocomposites (graphene (G), reduced graphene oxide (rGO) and graphene oxide (GO) for fuel cell applications.

Thus, this research project aims the development of transition metal/graphene based nanocomposites synthesized by electron beam or gamma irradiation for the following application: i) supercapacitors and as catalyst for purification of H₂ rich mixture, resulting from ethanol or methane steam reforming after water-gas shift reaction, by the preferential oxidation carbon monoxide reaction (PROX-CO) and supercapacitors.

**Work Plan**

- We propose in this study to evaluate the effect of the dose rate, cumulative dose on the uniformity of the shape and size of the nanoparticle on graphene based nanomaterial.
- It is also proposed to compare the efficiency of gamma ray and electron beam on the metal nanoparticule/graphene based composite preparation.
- Study of the electrochemical behavior of Ni/rGO, Pd/rGO, Au/rGO, Ni/G, Pd/G and Ag/rGO for supercapacitor application.
- Study of the catalytic properties of NiO/GO, Au/GO, Ag/GO and Pd/GO for PROX-CO process.

**EGYPT**

Radiation technology is an industrially available technology with a potential application in the field of material nano structuring. Ionizing radiation can be used to reduce metal ions like silver into nanometal. The most frequently used approach to prepare dispersion of metal nanoparticles involves the entrapment of metal cations within polymer chains followed by reduction with gamma rays. Radiation dose greatly affects the metal particle size at constant amount of polymeric stabilizing agent and metal salt.

Graphene is a true wonder material and has the potential to generate disruptive technologies. Reduction of graphene oxide (GO) into graphene (GIG) was conducted using gamma radiation. The presence of •OH radical scavenger and/or capping agent was crucial for the completion of GO reduction by gamma radiation. Graphene prepared by gamma-irradiation and its composite with polymer and organic inhibitor could be used for corrosion protection of metals. In addition, GO was used to enhance the mechanical properties and radiation resistance of some natural occurring
materials like artifacts. Moreover, the GIG and GO can be applied to enhance the mechanical and barrier properties of some materials used for packaging.

Nanogels based materials which are the key points to design a drug delivery system effectively and have high drug loading capacity, biocompatibility, and biodegradability have been successfully prepared from hydrophyllic polymers like polyvinylpyrrolidone and polyacrylic acid (PVP/PAAc) via gamma radiation-induced polymerization. Particle size and swellability of the prepared nanogels can be controlled through feed composition and concentration, polymer molecular weight as well as irradiation dose, temperature, and atmosphere. These nanoparticles are expected to be potentially useful in dry eye syndrome treatment, in delivering dopamine DA across the blood brain barrier (BBB) of Parkinsonian disease, in improving pilocarpine stability and bioavailability, and biological activity for acne symptoms treatment. Nanogel based materials like polyethylene oxide and polyacrylic acid (PEO-PAAc) Nanogels conjugated with folic acid were labelled with 99mTc and can be used for the detection of cancer.

On the other hand, nanoscale-surface modifications could be achieved by radiation grafting technique followed by chemical deposition of nano-metal, metal oxide or nano-scaled functionalized organic materials within radiation grafted polymers. Electroless plating of metal onto polymeric surface is a way to produce such metalized polymers. Thin film formation of ZnO onto polyolefin grafted surface make it good candidate for using as a catalyst, or in microelectronics packing technology. Polyaniline (PANI) thin film could be also synthesized by in situ polymerization onto poly acryllic acid grafted polypropylene films. Colour conjugated PANI-functionalized polymeric films could be used as a simple and safe food spoilage sensor.

Ionizing radiation can be used to prepared and modified nano-composite materials. PANI–TiO$_2$ nano-composites were prepared by ’in situ’deposition oxidative polymerization of (PANI). The introduction of PANI greatly enhanced the photocatalytic activities of the TiO$_2$ photocatalysts. Gamma irradiation was found to enhance the photocatalytic activity of the prepared PANI–TiO$_2$ nano-composites toward some organic dyes under visible light irradiation. Nano-composites films based on natural matrix was reinforced with clay and exposed to 10 kGy gamma irradiation to enhance the cellulose acetate film / Clay compatibility for use in packaging purposes water vapour transmission rate (WVTR) and oxygen transmission rate (OTR) of composite films was improved compared to pure cellulose acetate.
FRANCE

Radiation-induced elaboration of nanocomposites in dimensionally controlled macro- or micro-structures.

Additive manufacturing methods, particularly 3D printing are predicted to grow rapidly and substantially, in many sectors of industry. The current development of cheaper and highly performant production equipment as well as the large offer in starting materials result in a considerable increase of number of end-user industries exploiting these technologies.

3D printing includes various types of iterative and computer assisted elaboration of three-dimensional objects by joining powder grains or solidifying reactive or meltable materials typically layer by layer. The precision, repeatability and processable starting material are still key challenges. In addition, the technology suffers from some limitations in terms of intrinsic mechanical performance and from the need of additional functionality for the 3D materials. Various domains of application, such as biomedical devices, microfluidics, electrooptics, measuring instrumentation and sensorics, are expecting new technological developments to meet their current needs.

Based on the previous experience of our Institute in radiation processing of nanoparticles, nanocomposites and nanostructured materials, we will contribute to the CRP by combining radiation-induced chemistry and 3D printing with various approaches to improve the mechanical performances and/or to impart additional functionalities through a rational use of radiation processing, structuring or modifying materials at nanoscale.

The proposed research activity aims at studying the potentiality of radiation processing for the synthesis of nanocomposites forming or included in 1D to 3D structures (i.e. 1D: line, fibre or bar, 2D: grid, mesh, mosaic substrates, 3D: scaffold, prepared by molding, by lithography or by 3D printing).

Various types of chemical reactions will be considered and implemented, depending on the orientations of collaborative actions within the CRP:

- grafting reactions (from /onto) inorganic or organic nanoparticles,
- cross-linking polymerization of monomer blends including metal or inorganic nanoparticles,
- radiation-induced formation of nanoparticles by in-situ reduction (e.g. metal ions or graphene oxide) on the properties of organic nanocomposites including cellulose nanowhiskers or carbon nanotubes particles.

- polymerization-induced phase separation under ionizing radiation in blends of thermoplastic polymers dissolved in multifunctional monomers for producing tough networks resistant to crack propagation.

The diverse synthetic reactions listed above constitute an effective toolbox for elaborating nanocomposites constituting or included in structured materials (1 to 3 D, as defined above). The functionalities associated with the nanocomposites may relate to some specific features such as optical properties, electrical or thermal conductivity, stimuli responsiveness, fire-resistance, biocompatibility, etc.

INDONESIA

Synthesis of nano Chitosan-Microbial Cellulose (CH-MC) Composite for Splint Teeth in Periodontal Application

Health Research and Development Agency, Ministry of Health Republic of Indonesia reported that the prevalence of tooth and mouth disease in Indonesia in 2013 is 25.9%. Chronic periodontitis and tooth mobility are about 8% of the totals tooth and mouth diseases. Periodontal disease is considered an infectious pathology caused by the interaction between a susceptible host and bacterial factors present in dental plaque. Periodontal disease can cause Reduction of periodontal attachment which result in tooth mobility and migration, causing misaligned occlusal forces that hinder the balance between bone resorption and bone remodeling and the reorganization of periodontal fibres. Tooth mobility can be defined as visually perceptible movement of the tooth away from its normal position when a light force is applied or movement of a tooth in a horizontal or vertical plane of space. Tooth mobility usually is the result of occlusal trauma associated' with periodontal disease. One of the techniques to immobilize and stabilize the injured teeth is by splint periodontal. Splint can be a rigid or flexible device that maintains in position a displaced or movable part. Fiber reinforcement materials such as glass fibers and polyethylene fibers are being used in splinting technique. Currently there are a number of fiber reinforcement materials available on the market. Among them are glass fibers and polyethylene fibers. In Indonesia, these materials
have expensive price which is USD 50 to 150 per piece which make inaccessible for the poor people and most of these products are imported product. The initiative to prepare splint material from natural polymers such as chitosan and cellulose microbial is proposed in this project. It is hope that by using these materials and radiation technology to induce low molecular weight (LMW) chitosan and sterilized the product as well, it can reduce the price and can be a product substitution import.

Microbial cellulose (MC) or bacterial cellulose is an exopolysaccharide produced by various species of bacteria, such as Acetobacter, Agrobacterium, and Aerobacter. MC is preferred over the plant cellulose as it can be obtained in higher purity and exhibits a higher degree of polymerization and crystallinity index. It also has higher tensile strength and water holding capacity than that of plant cellulose. The typical Young’s modulus of MC is found to be in the range 15–35 GPa, with the tensile strength in the range 200–300 MPa. MC exists as a basic structure known as microfibrils, which are composed of glucan chains interlocked by hydrogen bonds so that a crystalline domain is produced. Fibrils of bacterial cellulose are about 100 times thinner than that of plant cellulose, making it a highly porous material and surface area, which allows transfer of antibiotics, chitosan or other substances. Besides having excellent properties, MC has the disadvantage such as does not have anti-bacterial and anti-inflammatory properties.

Chitosan [poly(1,4)-/β-D-glucopyranosamine], a natural polysaccharide, which is widely present among marine and terrestrial invertebrates. Chitosan could normally be obtained from crab or shrimp shells, by alkaline deacetylation of chitin. This biopolymer has a number of chemical and biological properties such as antimicrobial, anti-inflammatory and anticancer that makes it suitable for biomedical applications. It was reported that low molecular weight (LMW) chitosan showing higher activity to bacteria and mold compared to high molecular weight. High energy irradiation such as gamma rays and electron beam are an effective tool for preparing LMW chitosan. Chitosan nanoparticles can be prepared by ionic gelation method using Tripolyphosphate (TPP) as crosslinking agent. From these properties of MC, nano chitosan could be incorporated into the MC structure and induced a composite which can be used as splint material in periodontal application.
ITALY

The development of advanced and innovative food packaging materials able to increase the shelf life of packaged products and to reduce food waste is of utmost importance and also can be regarded as one of the main challenges to address the NO HANGER Sustainable Development Goal.

From a general point of view, in fact, access to sufficient, safe and nutritious food is a fundamental human right. According to the FAO, in order to meet the food demand of a global population projected to reach over 9 billion by the year 2050, a 70% increase in global food production is necessary. This increase has to be met in the context of resource limitation, food safety risks and environmental impacts. Thus, it will be crucial not only to increase food production but also to protect the food that is being produced, processed and distributed by developing innovative solutions that bring together the growers, processors, distributors and retailers. Food supply chains play a key role in this process and, specifically, food packaging is one of the critical nodes. Indeed, it is pivotal in the food chain since it has the vital task of containing food and retaining food quality and safety at each step as it moves through the supply chain to the consumer.

The principal aim of the 4-year agreement research project NANORADxPACK in the framework of the CRP F22070 is to assess through an experimental approach the relationship between nanotechnology, radiation application and processing and properties of innovative polymer nanomaterials for food packaging.

Two research groups are already involved in the project: The National Research Council (CNR) of Italy through the Institute of Polymers, Composites and Biomaterials (IPCB) and the National Reference Center for the Detection of Radioactivity in Feed and Foodstuff, Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata, Foggia (Italy). The two groups have complementary expertises in the field of polymer nanocomposites for food packaging and food irradiation. However, the project will be developed through strong collaborations with other institutions partners of the CRP. Moreover, also other research groups with further complementary expertises will be involved in the research activities, mainly food scientists, biologist and microbiologists in order to assess the effectiveness and possible use of the developed materials as active food contact materials.
JAPAN

Along the recent progress of nanotechnology, preparation of functional nano-objects with well-defined shape and orientation has attracted much attention. Methods to access such nano-objects are briefly categorized into bottom-up or top-down technologies. Controlled self-assembly of elaborately-designed molecules (bottom-up) gives well-defined nano-structured materials. However, it is difficult to perfectly expect how the molecules with the particular structure self-assemble into a certain nanostructure. On the other hand, top-down technology enables more general approaches, if the proper methodology is once established.

Our proposal is focused on our unique method, referred to as “Single particle-Triggered Linear Polymerization (STLiP)” technique, yielding wire-shaped nano-objects with controlled length and number density by just tuning the thickness of the target thin films and fluence of the incident high-energy ion beams, respectively. High-energy particles give their kinetic energy to a limited nm-sized spatial area along their trajectories, affording insoluble nanogels (nanowires) via polymerization and cross-linking of the materials. By reducing the fluence of the irradiated swift heavy ions (e.g. 490 MeV $^{192}$Os, 350 MeV $^{129}$Xe) under ca. $10^{11}$ cm$^{-2}$, we can avoid the overlap of the ion tracks. Also, the reactivity of the monomers and choice of solvents for developments are the key factors to obtain nanowires in this method. To the best of our knowledge, there is no general technology to obtain such nanowires (< 10 nm in diameter) from organic materials since “single” particle is the smallest unit as a tool to fabricate the materials. Considering the recent our finding that the small molecules is available as a target thin films for STLiP method, there is no longer any doubt about the importance of our proposal to develop a general technology to afford nano-sized objects from π-conjugated functional small-molecules.

Work Plans

• Establishment of vertically-aligned (standing) organic nanowires by irradiation of the organic films with swift heavy ions and following sublimation of the non-irradiated pristine regions.
• Fabrication of carbon nanowires by the protocol below.
  (i) Halogenated aromatic hydrocarbon compounds are efficiently polymerized within the ion tracks triggered by the irradiation with high-energy charged particles.
  (ii) The remaining non-polymerized parts are removed by development or sublimation.
  (iii) Calcination of the resultant nanowires to further form C–C bonds and release terminal H and halogen atoms.
• Development of superhydrophobic surfaces with continuous organic pillars.
  (i) Organic films on a substrate are irradiated with high-energy ions with high fluence to allow
      the overlaps of the ion tracks.
  (ii) The remaining non-polymerized parts are removed by sublimation.
  (iii) The isolated continuous pillared organic part may keep its vertical alignment to the substrate,
       which leads to the structured surfaces that would be an effective superhydrophobic surface.
• Development of nano-porous organic films used for sensing applications.
  (i) To search the conditions (selection of materials, ions species, and its energy), where bond
      breakings are dominant rather than polymerization by charged particle irradiations.
  (ii) Based on the condition (i), the fragmented molecules in the ion tracks are removed by
       development or sublimation, and a nano-porous film is obtained.
  (iii) Analytes can absorb the surface of the pores and selectively interact with the surface
       depending on the chemical structures of the analytes and surface.

KAZAKHSTAN
Ionizing radiation induced effects on properties and structure of metallic nanostructures with great
potential applications in optoelectronics, photoelectrochemistry, catalysis; medicine, etc. have
attracted considerable attention during the last few decades. Among the different types of ionizing
radiation, swift heavy ion irradiation using high electronic excitation is one of the promising
techniques used to control the size, shape, crystallinity, and hence the physical-chemical properties
of nanostructured materials and nanocomposites.
DC-60 heavy ion accelerator was launched in 2006, in Astana and is dedicated for applied and
fundamental research using beams of accelerated ions from lithium to xenon with energies from
0.34 to 1.77 MeV per nucleon, as well as for experiments on the channel of low-energy ion beams
received from an electron cyclotron resonance source with extraction intensities of up to 25 kV.
The cyclotron is supplied with three accelerated beam channels. Each channel is provided with set
of equipment to solve certain tasks, while one channel is assigned for specialized production of
track etched membranes
The main research areas are related with the development of track-etched membrane technologies:
- The use of track-etched membranes in water purification processes: filtration, membrane distillation and forward osmosis.
- Membranes functionalization
- In the field of nanotechnology: template synthesis of highly ordered nanostructures arrays and its application in catalysis and medicine.
- Fundamental and applied research of the radiation-induced modification of metallic nanostructures and ceramics.

RELATED PUBLICATIONS:


KOREA, REPUBLIC OF

Dr. Kim, ARTI, KAERI

Radiation technology has become a core technology in the analysis and synthesis of nanomaterials in Korea. The development of nanomaterials in Korea is subdivided into three research themes, such as advanced IoT (Internet of Things), eco-friendly and healthy people. Advanced Radiation Technology Institute (ARTI) as a branch of Korea Atomic Energy Research Institute (KAERI) is conducting the researches on nanomaterials in various fields such as electronic materials and biomaterials using electron beam accelerators and gamma irradiation facilities. Our team is conducting the researches related to the electronic devices such as solar cell, batteries, electromagnetic (EM) wave shielding, and thermoelectric materials. We introduce EM wave shielding materials for the first year, thermoelectric materials for the second year, and spintronics materials for the third year. Among these research themes, this report will briefly introduce the development of EM shielding materials.

As the performance of electronic device improves, the frequency used in it is also increasing. The radio frequency used in our lives is between 1 and 2 GHz and is expected to increase further. There is a need for an appropriate shielding material due to problems such as interaction of electromagnetic waves between the equipment and influence on the human body. Studies using nano materials are going to increase the resonance frequency of the shielding materials. We will study the application of uniform and high purity nanomaterials synthesized by radiation technology to electromagnetic shielding materials. This material group will start with an iron oxide system and its resonance characteristics at high frequency will be discussed.

Dr. LEE S. and others, KOMAC, KAERI

Status of development on swift heavy ion beam in Republic of Korea.

Ion beam radiation processing has been employed in membrane production due to its characteristics such as high linear energy transfer and Brag peak. Since 2010, as a part of World Premier Material project, an intelligent membrane material project has been established, and R&D and commercialization of multifunctional polymer membrane material are under way. However, this did not include Track-Etched Membrane (TEM) related researches yet and currently there are
no suitable ion beam irradiation facilities for the TEM production in Korea. Rare Isotope Science Project is on progress to build RAON (a heavy ion accelerator) by 2021. The Korea Multi-purpose Accelerator Complex (KOMAC) as a branch institute of KAERI operates a 100 MeV proton linac and various ion beam facilities and has been under beam services since 2013. KOMAC attempted preliminary studies of TEM production using proton beams. Their results showed that pores were formed on the surface of the polymer membranes and with the UV exposure, depth of the track channels got deeper through the membrane. At present, KOMAC is developing a compact 1 MeV/n Radio-Frequency Quadrupole based ion beam accelerator. Ar ion beams till +16 charge states were extracted and expected to generate Kr ion beams. Once these ions are accelerated as Swift Heavy Ion (SHI) beams, it will be highly effective in forming ion tracks completely through the polymers. By controlling SHI beam species, dose, irradiation time, etching time and UV radiation time, TEM can be formed depending on a range of applications such as filtration, separation, bio-sensing, fuel cell etc. Development of SHI beam production for TEM will provide a core technology for advanced membrane material which can be used in particulate matter filters and water treatment filtration which are essential in day-to-day life.

MALAYSIA
Following Malaysian government’s plan in diversifying her energy sector, renewable energy has been given a significant emphasis in Malaysia’s energy policy to meet the country’s energy demand. Among this, hydrogen fuel cell has been identified as one of the emerging technologies for Malaysia’s well-beings, wealth creation and governance in 2015 – 2050. Contrary to other energy generation methods, fuel cells have minimal wastes, environmental, social and geographical issues associated with their applications. Switching to fuel cell technology is, therefore, a wise decision, especially for automobile industries, as it has the advantage of zero carbon emission and high energy conversion efficiencies. This is in support of the United Nations Climate Change Conference commitment in reducing CO₂ emission by 45% by 2030 besides in line with the Malaysia National Automotive Policy (NAP) 2014 initiative in developing a regional automotive hub for energy-efficient vehicles (EEVs). However, the high cost of fuel cell technology has been the main hindrance to the implementation and commercialization of fuel cell technologies. This owes mainly to the use of precious metals such as platinum as electrocatalysts. The development of cost-effective and highly efficient non-precious materials as the
electrocatalysts for fuel cells is thus imperative for fuel cell technology to be economically viable. The present study aims to develop a nano-electrocatalyst system based on graphene supported non-precious metal oxides, with performance comparable to the precious metal electrocatalysts system. This can be achieved via microstructural modification and defect engineering using radiation techniques. Electrocatalysts of nano sizes have the advantage of increased exposed surface areas available as the active sites for catalytic reactions and by irradiating these materials with appropriate dosages of radiations, microstructural change and defect sites favourable to catalytic reactions could be created. Physico-chemical and electrochemical characterizations will also be performed to study the structure-property relationships of the nano-electrocatalyst system. Findings from this study are beneficial to both the technological and economic aspects of renewable energy industries.

**Work plan**

- Fabrication and characterization of nano-electrocatalyst system based on graphene supported non-precious metals oxides.
- Structural modifications and defect engineering using radiation techniques.
- Determination of the optimal irradiation parameters for enhanced electrocatalytic performance.
- Identification of the active sites for oxygen reactions and evaluation of the catalytic mechanisms involved.
- Performance testing of the irradiated nano-electrocatalyst system in fuel cell modules.

**MOROCCO**

Morocco imports 97.5% of energy to fulfill its need. Energy is considered as a driver agent for major projects launched in all sectors: Tanger Med, Emergence, Off-shoring, Azur Plan, Green Morocco Plan, Cement, social housing, new industrial zones…

The energy sector, particularly renewable energy, is among Morocco's national priorities expressed in the national energy strategy and the national priority research programs since 2009. Thus, many institutions have been created in last decade such as MASEN (Moroccan Agency For
Solar Energy) in 2010 and IRESEN (Institute of Research in Solar Energy and New Energies) in 2011 as support the national energy strategy and committed to the development of renewable energies and have established programs encompassing research themes through calls for projects. Developing new materials by several Moroccan research teams to reach the goal is become crucial and was the priorities of these institutions. Research in this context has led to promising results in recent years. However, the materials developed were obtained via conventional chemical or physical processes or reaction (CVD, PVD,.......). The process of implantation of ion by using radiations from accelerator is absent whereas the other means of characterization exist there. The use of nuclear sources and facilities of our partners was considered.

PHILIPPINES

Current electron beam- and gamma-radiation grafting activities in the Philippines consist of development of (1) adsorbents for dyes, heavy metal ions and rare earth elements, (2) transesterification catalyst for biodiesel fuel production and (3) modified polymeric membrane for fuel cell application. Polypropylene in nonwoven fabric or membrane form was used in the preparation of these materials. In each case, the dependence of degree of grafting (Dg) on different grafting conditions, i.e. absorbed dose, monomer concentration, monomer-to-surfactant ratio, and reaction time, was optimized and systematically studied. Radiation-grafted adsorbents characterized by relatively high adsorption capacities for chromium, cadmium, lead and mercury were prepared and evaluated using both batch and dynamic systems. The radiation grafted adsorbents were found to be effective in the treatment of actual tanning industry and laboratory waste waters. A transesterification catalyst which could be used for at least seven times was also successfully prepared through the radiation-grafting technique. In addition to these studies, a collaboration was forged with a university professor who has expertise in surface plasmon resonance (SPR) spectroscopy technique. The collaboration will deal with the modification of the gold substrate by radiation-induced grafting for SPR sensor application. The preparation of a graft copolymer through a technique that combines the merits of radiation-induced synthesis and reversible addition-fragmentation chain transfer (RAFT) process in emulsion phase was also investigated. We demonstrated the facile combination of these techniques in a simple reaction that ultimately results in the fabrication of copolymer with immobilized
epoxide groups on the surface. The preparation of graft copolymers through a method that combines the advantages and merits of radiation-induced grafting in water-based emulsion, an environment friendly green method, and controlled radical polymerization via RAFT-mediation was successfully performed. Both electron beam- and γ-radiation initiation processes were used in the synthesis. While conventional graft polymerization in emulsion phase yielded graft copolymers with low degree of grafting values even at high absorbed doses, addition of RAFT agent to the graft polymerization system allowed the synthesis of polyethylene/polypropylene-g-poly(glycidyl methacrylate) (PE/PP-g-PGMA) with more tunable degree of grafting by controlling the grafting parameters. Relatively good control (PDI ~ 1.2 for selected grafting conditions) during polymerization was attained. The number average molecular weight of free homopolymers increased as a function of monomer conversion. NMR analyses of the free homopolymers indicate the presence of dithiobenzoate group from 4-cyano-4-((phenylcarbonothioyl)thio) pentanoic acid RAFT agent on the polymer chain.

POLAND

Studies related to radiation synthesis and/or modification of nanomaterials at the Institute of Applied Radiation Chemistry (IARC), Faculty of Chemistry, Lodz University of Technology, have been initiated over 30 years ago. Initially they were focused mainly on supramolecular systems (studies on micellar and other nanoheterogeneous systems). Since 1998 we have initiated studies on synthesis of polymer nanogels by radiation-induced intramolecular crosslinking of individual polymer chains. This method has been initially tested on simple, neutral water-soluble polymers, and later proved to be also applicable to more complex systems as thermo-sensitive polymers, polyelectrolytes and H-bonded interpolymer complexes. This approach is now used in a number of leading radiation chemistry labs. Further studies on intramolecular recombination of polymer radicals have been performed both experimentally and using Monte-Carlo simulations and resulted in better understanding of the underlying processes as well as in refinements allowing for better control over product properties. Another aspect of radiation synthesis of nanomaterials studied at IARC has been the synthesis of gold nanoparticles, using ionizing radiation as a source of reducing species and polymers and oligomers as stabilizing agents. In parallel, we have studied analogous
processes initiated by ultrasound. Overall, these two topics have been the subject of 26 papers and 2 book chapters published by IARC within the last two decades.

PORTUGAL
The radiation processing of hybrid materials (HMs) is already an alternative to the current sol-gel process, given opportunity to the development of different properties and functionalization’s not easy to access through the traditional way of preparation. Bioactive PDMS-TEOS-ZPO (polydimethylsiloxane - tetraethylorthosilicate - zirconium propoxide) hybrid materials for biomedical applications (bone cements) and with biocide activity are successful examples of HMs prepared through gamma irradiation.

Although, the severe conditions of radiation processing (high dose-rates and absorbed doses) needed for the preparation of hybrid materials confine the possibilities to go further in the development of new properties and functionalization’s of these type of nanostructured materials. The introduction of ionic liquids (ILs) in HMs precursor’s composition could be a solution to overcome this problem. Their special capability to dissolve, at the same time, both organic and inorganic solutes assisting the copolymerization reaction of the PDMS could be of crucial importance in a synthesis involving TEOS/ZPO and PDMS. Our main objective is thus to test a new approach in the radiation processing of nanostructured HMs taking advantage from the “best of two kingdoms”: ionizing radiation and ILs. The influence that ILs cause in the necessary doses, dose rates and specific conditions of irradiation will be studied in order to make specific tailored hybrid materials more accessible and affordable. Simultaneously, the development of high demanded and/or special functionalizations will be considered, trying to extend by this way the range of applications of this type of materials.

Work plan
- Selection of an efficient and toxicologically safe group of the most adequate and promising ILs, regarding the chemical nature of the precursors (chemical compatibility) and the intended final nanostructure of the hybrids.
- Evaluation of the ionizing radiation effected on the selected ILs.
- Evaluation of the ILs effect of on the radiation dose to attain the PDMS non-flowing gel point.
• Definition of new irradiation parameters and optimization of the method to prepare PDMS-based hybrids through radiation processing assisted by ILs.
• Evaluation of the effect of the ILs on the molecular organization of the new hybrids and consequently on their final properties.
• Explore the new possibilities of functionalization of the PDMS-hybrids for specific applications (mainly for biomedical and environmental applications) by radiation processing assisted by ILs.

RUSSIAN FEDERATION

Development of versatile nanotechnologies based on using radiation processing, including production of track-etched membranes and nanocomposites is carried out at several institutions in Russian Federation. The research activity in the Laboratory of High Energy Chemistry at Lomonosov Moscow State University (LHEC MSU) is focused on development of efficient methods for fabrication and modification of metal-polymer nanohybrid materials for various applications. Different-type materials were synthesized by the radiation-induced reduction of noble and transition metal ions in polymer solutions, suspensions and swollen films. Recent development is concerned with the introduction of a new approach based on application of relatively soft X-rays (10 – 50 keV) for spatially selective and highly efficient formation of metal nanostructures in polymer matrices. The key point of this approach is selective absorption of the X-ray photons by heavy elements, which provides strong local enhancement of the radiation-chemical processes in the vicinity of metal clusters and nanoparticles dispersed in an organic or polymer medium. The effect may be tuned due to variations in nanoparticle size, photon energy and system organization.

Application of this technique made it possible to prepare the nanohybrids with different size and spatial distribution of metal nanoparticles and, in particular, to obtain the materials with selective localization of nanostructures in the surface and sub-surface layer to be used for fabrication of catalysts, biosensors, and bactericide materials. As an example, cotton fibres with ultrathin interpolyelectrolyte coating was efficiently modified by nanoparticles to yield a material with stable antimicrobial activity. Also, a “one-pot” radiation-chemical synthesis of nanohybrid starting from monomer solution with simultaneous polymerization and metal ion reduction was performed.
Further development of this approach may provide a common basis for new versions of the radiation-chemical nanotechnology to produce functional materials. Also, it can be potentially applied for obtaining of stable protein-coated metal nanoparticles for potential applications in medicine and teranostics.

Selected related publications:


SERBIA

Project HYDROBOT aims to develop novel soft electronic hydrogel nanodevices based on gold nanoparticles, poly(N-isopropylacrylamide) and poly (vinyl alcohol) (Au/PNIPAm/PVA) using γ-irradiation technology. Main goal of HYDROBOT is to explore areas of radiation technology, with insight into easily, efficiently and cheaply modifying polymer/metal constituents to produce soft electronics for information technology application. Radiation technology inclined to advanced soft nanoelectronics open up new strategy to manipulate with advanced functional materials into hybrid
3D nano-environment suitable to change rigid silicone-based hard electronics. During the past decades, the development of electronic devices has focused on overcoming the technical limitation of inorganic electronic devices to achieve high-performances with faster operating speeds and larger storage capacities in smaller sizes.

The global electronics materials and chemicals market is expected to reach USD 81.05 billion by 2024. Nowadays, paradigm of technological convergence for future electronics has been progressing towards human-friendly technology which considers ease of use, wearing sensation, portability, human sensibility and smart communication with surrounding environment. The increasing interest in the use of unconventional multifunctional nanomaterials in electronics requires new technological advancement which can successfully undergo reversible, flexible and programmable deformation of actuators that will significantly reduce the total cost of global production.

The development of nanocomposites based on γ-irradiated polymer/metal constituents, already gave contribution to electronic sensor devices with a number of innovative approaches in optics, magnetics, catalyst and environmental monitoring, but still there is no deep insight into programmable designing of local stimuli-responsive sensibility of nanocomposites. In order to develop soft nanodevices, ubiquitous electronic research requires advanced methodology to improve paradigm of chemistry and processing, combine to produce nanostructure, which in turn determines the diversity of material requirements, short development time scale and focus on the cost.

**Work plan**

- Radiation-chemical synthesis, characterization and optimization of photothermal potential of AuNPs/PNIPAM/PVA hydrogel nanocomposites.
- Exploring photo/thermo/mechanical potential of AuNPs/PNIPAM/PVA hydrogel nanocomposites for soft electronics.

**THAILAND**

The proposed research is focused on molecular template design for nanostructure synthesis, modification and fabrication of nanostructure materials using radiation-controlled processes.
Irradiation techniques based-on top-down (i.e., degradation or chain scission) and bottom-up processes (i.e., crosslinking, polymerization, curing, grafting and reduction reaction) have been performing for nanofabrication (i.e., metallic nanoparticles, amphiphilic core-shell nanoparticles, hybrid nanoparticles, nanoparticles networking, nanowhisker/nanofiber, nanocomposite, nanoporous and nanogels). Although the synthesis and fabrication of nanostructure materials using radiation techniques have been studied and some processes have been established, it is still important to further strengthen capacity of the effective and competitive irradiation techniques for nanofabrication of new and value-added materials for industrial application. Basically, both single irradiation technique and combined appropriated techniques have been manipulated and designed to achieve the desirable diverse nanostructures. The targeted applications of the radiation-controlled nanostructures will be for industrial purposes, such as functional coatings/printings (e.g., superhydrophobic and antimicrobial coatings, conductive inks), cosmeceuticals (active and antioxidant encapsulated nanoparticle, active compound entrapment nanoparticles) and agrochemicals (e.g., fertilizers and active compounds entrapment, moisture retention). The radiation-developed nanostructures include 1) Polymer-stabilized-metallic nanoparticles for coating/printing or cosmeceuticals, 2) Hydrophobic polymer shell modified SiO2NPs for coating/printing, 3) Polymer shell-grafted-SiO2 NPs for metallic NPs immobilization for coating/printing, 4) Polymeric shell-grafted-GO NPs for metallic NPs immobilization for coating/printing (conductive inks), 5) Interpolymer complex nanogels (IPC NGs) for active compound entrapment for coating/printing (high performance ink), cosmeceuticals and agrochemicals, 6) Polymer core-shell nanoparticles for active compound entrapment for cosmeceuticals and agrochemicals, 7) Interpolymer complex nanoparticles (IPC NPs) for active compound entrapment for agrochemicals and 8) Hydrogel template for nanostructure fabrication as smart agrochemicals and 2D/3D printing materials. Scientific approaches for the synthesis and fabrication by controlling parameters under irradiation process will be studied to achieve optimizing conditions and protocols. Nanostructure and its performance based on proper applications will be included in the scope of work. Besides scientific data studies, it is also important to note that the studies on simplifying the protocol and process in terms of simultaneous synthesis and fabrication systems will also be considered for target industrial approach of the country (i.e., Food & Agriculture, Health & Wellness, and Digital & IoT).
TURKEY

Laboratories for Radiation & Polymer Science (LRPS) of the Department of Chemistry of Hacettepe University is one of the best equipped & staffed polymer research laboratories in Turkey. Research in LRPS is broadly organized around Polymer Chemistry and Radiation Chemistry, including a number of subareas such as synthesis, characterization and modification of polymers, hydrogels, membranes and adsorbents, controlled/living polymerization techniques, nanostructuring of polymers, radiation-induced synthesis of polymers, copolymers and hydrogels, radiation-induced crosslinking, degradation and grafting. LRPS has aqueous and organic GPC systems, a wide range of spectrometers including FTIR, Uv-Vis, Luminescence, Pulses NMR and Positron Annihilation Lifetime (PAL), thermal and mechanical analyzers, processing equipment such as rheometer, extruder, mixer, pressing and rolling off systems, contact angle goniometer, AFM, Zetasizer and other laboratory infrastructures necessary for the synthesis of polymers and copolymers. Many research activities have been carried out by LRPS under the framework of IAEA Coordinated Research Project and over the years numerous collaborations have emerged from this program and evolved into new joint ventures.

UNITED KINGDOM

Nanotechnology has been hailed as one of the groundbreaking technologies providing innovative solutions to society’s greatest challenges. Nanotechnology is a core component in production of new advanced products spanning across medicine, healthcare and bio-imaging, water purification, barrier coatings, chemical catalysis, energy storage, sensing, among many other. As stated in the “Global Markets for Nanocomposites, Nanoparticles, Nanoclays, and Nanotubes” (2017) report “…the global nanocomposite market, in value terms, should reach $5.3 billion by 2021 from $1.6 billion in 2016”. It is estimated that the UK accounts for about 5-15% of the international nanotechnology market; hence, it is of prime national importance for the United Kingdom to maintain and strengthen its strong position in the field in order to win in global competition.

For the UK, it is quite difficult to estimate the exact value of the Government’s investment in nanotechnology as it is intimately integrated in so many areas of science and technology. As outlined in the "Nanotechnology: a UK Industry View” (2010) report the estimated Government support for nanotechnology in 1998–2010 has exceeded 640M£. Investments in nanoscience
research remain a key priority; in the past the Engineering and Physical Science Research Council (EPSRC) supported successful Nanotechnology Programme with current investment offered through the “Manufacturing the Future” theme. As a result of this significant EPSRC investment, the UK has shown an impressive progress in nanoscience, resulting in large body of high-quality research and commercial products enabled by nanotechnology. United Kingdom is currently enjoying the internationally leading position in this field; the proposed project for the IAEA’s 22070 CRP "Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology" aims to contribute directly to the existing UK’s excellence in nanoscience.

Work Plan
The research programme will be 4 years in duration, organised into three work packages (WP1-3). These work packages correspond directly to the research objectives outlined in the proposal report. More specifically, the research activities of WP1 will include two essential steps: (a) preparation of a dispersed reaction mixture containing a selected solvent, graphene template and metal ions via ultra-sonication; (b) "one pot" radiolytic synthesis of the supported metal NPs using optimised formulation.

WP1. Radiation chemical synthesis of supported Pd nanocomposites
The dispersion of graphene or graphene oxide into selected liquids will be achieved by ultrasonic. Graphene-supported metal nanostructures will be prepared using steady state gamma irradiation in the presence of precursor metal salts. In a typical experiment, in order to deposit monometallic nanoparticles on exfoliated graphene or GO sheets, graphene or GO dispersion mixed with appropriate amounts of palladium (II) salts will be ultra-sonicated until stable dispersions are produced. Prepared solutions will be purged with argon to remove dissolved oxygen. Obtained solutions will be irradiated using radiation from various sources. A total irradiation dose in the range of 30-100 kGy will be deployed to ensure complete reduction of metal ions and GO into metal NPs and rGO, respectively. After the reduction, formed nanocomposites will be precipitated by centrifugation and washed with ethanol. Finally, isolated nanomaterials will be dried at moderate temperature, e.g. 60°C, in a vacuum oven. The biggest challenge at this stage will be to establish (for each each "metal-carbon-solvent system) optimal synthetic conditions.
leading to the uniform and stable decoration of graphene templates with a few nm sized metal NP. Decoration of the graphene support with noble metal NPs and the average particle size of synthesised nanoparticles will be determined by X-ray Diffraction (XRD) analysis. The homogeneity of dispersion of prepared metal nanoparticles across the carbon support as well as the composition of individual metal NPs will be further characterised using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

**WP2. Characterisation of electrochemical properties of carbon-supported metal NPs**

Systematic investigation of electrochemical properties of prepared nanocomposites will be conducted using cyclic voltammetry. The working electrode will be prepared on the basis of Nafion-impregnated catalyst cast on a glassy carbon disk. The model reaction for the activity screening will be the oxidation of glucose into gluconic acid and hydrogen evolution reaction. The electrochemical surface area of noble metals in these nanostructures as well as the catalyst utilisation efficiency will be examined in order to evaluate the functional performance and stability of prepared catalysts. This assessment will identify nanomaterials with the most robust catalytic properties. Further characterisation of synthesised nanocomposites will be carried out. The metal content in all samples will be measured by Thermogravimetric Analysis (TGA). The oxidation state of formed metal nanonoparticles and potential radiolytic functionalisation of graphene matrix will be characterised by X-ray Photoelectron Spectroscopy (XPS). Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS), UV-Vis Absorption Spectroscopy, Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM) will be deployed routinely as complementary techniques for the analysis of formed nanocomposites.

**WP3. Using various ionisation sources for the synthesis of carbon-supported metal NPs**

Activities in the final phase of the project will build upon progress made in WP1-2. The work will focus on using alternative sources of ionising radiation (e.g. synchrotron photons, electron and ion beams) to produce metal NP-decorated nanocomposites. This study will elucidate the effect of Linear Energy Transfer (LET) on the structure and properties of the carbon-supported metal nanoparticles.
VIETNAM

Radiation technology in Vietnam was started in 1986 when a research Co-60 irradiator of 16.5 kCi was established in Dalat Nuclear Research Institute. There, Radiation Technology Department and Radiation Biology Department are the key units that exploited the radiation source for studying such as: radiation sterilization, food preservation and material modifications. A semi-commercial Cobalt facility with activity 110 kCi was set up in the Hanoi Irradiation Center (HIC) in 1991 for development demonstration of radiation technology in Vietnam. Next, a new period of application of radiation processing has been opened since an industrial irradiator project supported by IAEA in cooperation with Vietnamese Government has been put into operation in 1999, in Ho Chi Minh City – VINAGAMMA with 400 kCi activity. Main functions of VINAGAMMA including research and development of radiation technology. To provide radiation processing services such as sterilization of healthcare products, food irradiation and others. In 2012, the accelerator UELR-10-15S2 (10 MeV, 15 kW) has been put into operation and has been also used for purposes as Co-60 gamma source.

The research and development works have been carried out frequently in Research and Development Center for Radiation Technology – VINAGAMMA a unit belongs Vietnam Atomic Energy Institute (VINATOM). Degradation of natural polymers prepared the products such as OLICIDE 9DD, Zasa 3DD, STOP 5DD... are protectors and elicitors for plant. The water super-absorbent hydrogels of GAM-sorb P and GAM-sorb S are the results from studying cross-linking polymers by irradiation. Grafting functional monomers on natural polymers have been studied for absorption of toxic metal ions and colors from waste water. Lately, research and development of the nano and nanocomposite materials have been been also investigated. Reduction by irradiation for preparation of silver nano, gold nano is an effective method by formed nano cluster with the homogenous particles size without by-products of reductants. The antibacterial materials deposited silver nano particles (AgNPs) such as AgNPs/Ceramic composite for water treatment; the AgNPs/Fabrics against multidrug-resistant bacteria from the clinical specimens were tested.

In Vietnam, the aquaculture has been identified as a key economic branch with high export turnover. However, the use of chemicals to treat decontamination for the ponds of fish or shrimp usually leads on residue which is unsafe for human health. Nanotechnology plays an important role in providing new materials for water filtration and purification, and approaches to reduce the pathogenic bacteria for fish or shrimp in aquaculture system. Therefore, deposition of AgNPs...
on natural diatomite containing about 60% silica for preparation a “green” antibacterial nanocomposite has been necessary to substitute bactericide. Therefore, the research project concerning: “Preparation of Silver nano/Diatomite nanocomposite by irradiation method in order to treat the pathogenous bacteria for catfish (Pangasianodon hypophthalmus)” has been proposed for connection with CRP: “Enhancing the Beneficial Effect of Radiation processing in Nanotechnology – F22070”.

Work Plan:

- Study on effect of the physical and chemical factors (absorbed doses, concentration of precursor, binders) on the size and the content of Ag nanoparticles in nanocomposite of Ag nano/diatomite by EB irradiation
- Investigation of physico-chemical and structural characterizations of Ag nano/diatomite nanocomposite
- Testing antibacterial efficacy of Ag nano/diatomite nanocomposite against pathogenous bacteria for catfish (Pangasianodon hypophthalmus) in vitro and in vivo
- Estimation of influence of Ag nano/diatomite nanocomposite on water quality (pH, BOD$_5$, COD, total aerobic bacteria) as well as environmental toxicity LC$_{50}$ (Lethal Concentration) for catfish.
- Deposition the other metal nanoparticles (Cu, Zn) on diatomite in comparison with nanocomposite of Ag nano/diatomite
- Selection of standard data for development of metal nanoparticles/diatomite nanocomposite in order to substitute bactericide in aquaculture.

4. DISCUSSIONS

4.1. OVERVIEW OF THE PROPOSED RESEARCH ACTIVITIES

The primary goal of this CRP is to exploit innovative methodologies and technologies to fabricate high performance and high value-added nanoproducts for applications in electronics, energy,
environment and functional materials designed, among other various applications, for healthcare, food packaging and agriculture.

To reach this objective, the coordinated activities should be focused on

- the development of processes, techniques and protocols for radiation-driven nanofabrication of value-added products;
- investigations on key factors behind scientific challenges in radiation processing, such as structural and functional parameters, and methodological and technological aspects;
- strengthening the network of international collaboration in the field of radiation-driven nanofabrication.

The projects selected by IAEA among the proposals received to the call Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology (F22070) respond to these objectives with a valuable diversity of expertise and know-how.

In the perspective of the short-term transfer to industry of the achievements of the program, the main drivers for the research and development activities were discussed for 6 main fields of application, covering Environment, Electronics and Energy, Healthcare, Functional materials, Chemical Industry, Food and Agriculture (noted A to F).

Four classes of materials, noted 1 to 4, were considered: Metal nanoparticles, Grafted or surface-modified materials, Molecular platforms, encapsulants and polymer blends, nanostructured materials and dimensionally structured objects.
## Presentation of the research activities of the CRP in the form of a matrix by domain of application and class of nanomaterial.

<table>
<thead>
<tr>
<th>DOMAINS OF APPLICATION</th>
<th>(1) METAL NANOPARTICLES</th>
<th>(2) GRAFTED AND SURFACE-MODIFIED MATERIALS</th>
<th>(3) MOLECULAR PLATFORMS, ENCAPSULANTS, BLENDS</th>
<th>(4) NANOSTRUCTURED MATERIALS DIMENSIONALLY STRUCTURED OBJECTS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A) ENVIRONMENTAL APPLICATION</strong> (RADIONUCLIDES, POLLUTANTS, SENSORS FOR POLLUTANTS, CATALYSTS FOR DEPOLUTION)</td>
<td>D-metal NPs as catalysts for depollution</td>
<td>Modified Au substrates for SPR sensors</td>
<td>-</td>
<td>D-metal nanotubes for depollution; Nano TiO₂ / PANI for photocatalytic depollution; Chemical stable hybrid materials with biocidal activity; Track etched membranes</td>
</tr>
<tr>
<td><strong>B) ELECTRONICS AND ENERGY</strong> (SILICON MATERIALS, PHOTOTHERMAL)</td>
<td>Metal oxide NPs as electrocatalyst for fuel cells; Nanofillers for conductive inks for RFID/NFC tags; Metal NPs for soft nanoelectronics; Metal/graphene based nanocomposites (fuel cell and supercapacitors)</td>
<td>Nanoscale heterojunctions with nanowire assemblies; Extended defects by implantation techniques in thin films</td>
<td>-</td>
<td>Carbon based nanowires – Metal/graphene based nanocomposites (fuel cell and supercapacitors) – Si platelets formation for photovoltaics – stimuli responsive nanoelectronics</td>
</tr>
<tr>
<td><strong>C) MEDICINE, HEALTHCARE, COSMETICS</strong></td>
<td>Nanocarriers for radiotherapy, theranostics, antimicrobial nanocomposites; Metal NPs antimicrobial and cosmeceutical additives</td>
<td>Biocompatibility and biofunctionality by grafted nanolayers/ nanocarriers for tissue engineering; biomaterials and drug delivery</td>
<td>Nanochitosan/microbial cellulose blends for splint periodontal; Polymer NPs and nanogels for drugs, genes and radioisotopes encapsulation and release</td>
<td>3D porous scaffolds and bioactive hybrid materials for tissue engineering and for implants (consolidation, bioresorption, ...)</td>
</tr>
<tr>
<td><strong>D) CHEMICAL INDUSTRY, CATALYSIS</strong></td>
<td>Au-GO as catalyst for reforming PROx-CO process; Metal nanocatalysts for synthesis; Pd NPs as supported catalyst using surface grafting; ion track membranes with embedded metal nanotubes</td>
<td>RAFT mediated RIGP for the design of surface with controlled properties</td>
<td>Metal oxide nanoparticles for photocatalysis and electrocatalysis</td>
<td>Carbon supported Pd NPs for fuel cells and hydrogen evolution reaction</td>
</tr>
<tr>
<td><strong>E) ADVANCED FUNCTIONAL MATERIALS</strong> (COMPOSITES, PACKAGING, CULTURAL HERITAGE, COATINGS, MATERIALS WITH SPECIFIC PROPERTIES)</td>
<td>Use of diamonite for supporting metal NPs in nanocomposites; nanocomposites, soft materials and actuators with specific magnetic or optical properties; electrically conductive nanocomposites including nanotubes; Metal NPs in (thermally responsive) 3D-printed materials</td>
<td>Superhydrophobic surfaces modified with nanowires; Surface modified Fe₂O₃ NPs; Surfaces-modified nanofilbers for functional coatings and composites; Surface-modified cellulose NP in materials, including packaging films for food preservation</td>
<td>Nanogels and nanocarriers for pigment and active compounds entrapment</td>
<td>Hybrid materials for surface protection of stone-based cultural heritage artefacts; Graphene-based anticorrosion coatings; Electrically conductive nanocomposites including graphene or carbon NPs; Nanocomposites in 3D printed materials</td>
</tr>
<tr>
<td><strong>F) FOOD AND AGRICULTURE</strong> (ANTIBACTERIALS FOR AQUACULTURE ...)</td>
<td>Antibacterial Ag nanocomposites for aquaculture</td>
<td>Nanocomposite food packaging materials with improved mechanical and permeation properties</td>
<td>Nanoparticles for fertilizer and active compound entrapment; Superabsorbs based on natural/synthetic polymer network</td>
<td>-</td>
</tr>
</tbody>
</table>
The corresponding matrix shows that Energy and Electronics, Healthcare / Cosmetics, and Functional Materials represent the main domains of activities for this CRP. Environmental applications, Chemical Industry and Food and Agriculture, are secondary in relative importance, yet representing a very active and promising fields of investigation.

4.2. ANALYSIS OF SCIENTIFIC GAPS BY CLASS OF MATERIAL

One of the aims of this CRP is to address some of the specific scientific challenges regarding the most urging topics in the field of radiation-synthesized nanomaterials and to fill the knowledge gaps between the current state of the art and the emerging needs in application of radiation technology in nanomaterials and nanoprocessing. These scientific gaps and challenges include:

- Better understanding and better control of the key parameters in radiation processing of nanomaterials,
- Higher degree of control on morphological parameters of the radiation-synthesized nanomaterials,
- The need for simpler and more robust synthetic approaches
- Exploitation of the potentialities of natural polymers for the synthesis of nanomaterials
- Combine the unique features of nanomaterials with the dimensionality of the objects made thereof
- New methodological tools for advanced characterization and for simulation

The specific problems to be addressed within this CRP are developed below by class of nanomaterials.

4.2.1. Metal nanoparticles

The fabrication and modification of various functional materials including metal nanostructures for diverse applications should be essentially developed based on extensive collaborative research. This main goal of this research activity is to establish the key factors controlling the formation,
distribution and stability of the metal nanostructures of different morphology, their interaction with matrix and functionality.

The principal scientific challenges in this area can be identified as follows:

a. It is important to achieve precise control of the NP size and size distribution as well as their spatial distribution in the composites to get effective and reproducible tools for preparation of the materials with desirable functional properties. In order to optimize the radiation-induced synthesis of NPs the following specific issues should be addressed:

- Improving understanding of physical and chemical factors controlling the nanoparticle size, size distribution and morphology, extending the knowledge on kinetics and mechanism of NP formation in solutions and complex organized media;
- Development of the principles for manipulation with the spatial distribution and localization of metal nanoparticles in the nanocomposite matrices;
- Investigation of the effect of radiation parameters (radiation type, absorbed dose and dose rate) on the formation, localization and microstructure of nanoparticles (experiment and simulation) and intercomparison between the results obtained with different radiation sources;
- Introducing new approaches for fabrication and modification of nanoparticles and nanocomposites based on potentiality of X-rays in the energy range of 10 to 100 keV;
- Introducing new polymer matrices and solvents for synthesis of nanocomposites with specific nanoparticle size distribution, functional properties and stability.

b. A promising way of generation of metal nanostructures of different morphology for catalytic and other functional applications is associated with using confined media (like track-etched nanopore membranes) as templates for NP synthesis. Development of this approach is based on achieving the following specific goals:

- Securing knowledge of the peculiarities of the kinetics of formation and growth of metal NPs and nanostructures of various morphology in confined environment (in particular, in the track-etched membrane nanopores);
- Optimizing the electroless template synthesis approaches for improvement of the composite functional properties.

c. A crucial issue for optimization of the functional properties of nanocomposites and assuring their reproducibility is precise characterization of the materials by advanced physical methods and interlaboratory comparison of the structure and properties of the samples obtained by different participating groups. In order to achieve these goals, it is necessary to perform detailed investigations targeted on the following issues:

- Introducing new tools and procedures for in situ and ex situ characterization of structure, distribution and properties of nanoparticles
- Performing careful interlaboratory comparison to check the reproducibility of the radiation-induced synthesis of nanoparticles in order to establish a common procedure, which can be finally adopted a protocol.

d. One of the most important problems, which may lead to limitations in practical applications of nanocomposites incorporating metal NPs is related to their general instability determined by thermodynamical aspects and effects of aggressive environment. In order to overcome these limitations, the following scientific issues should be addressed:

- determination of the factors controlling stability of metal NPs in different matrixes and investigation of the kinetics of their ageing;
- development of the approaches to improve the stability of NPs and nanocomposites.

4.2.2. Grafted and surface-modified materials

Surface grafting and modification of polymeric materials is attracting increasing attention as it enables the preparation of new materials from known and commercially available polymers having desirable bulk properties like thermal stability, elasticity, permeability, etc., in conjunction with
advantageous newly tailored surface properties such as biocompatibility, biomimicry, adhesion, etc. Ionizing radiation is one of the most powerful tools for preparing surface-modified materials as it generates desirable functionalities, e.g. radicals on most substrates. The scientific gaps related to RIG and thin film preparation techniques are listed below:

e. An efficient and reproducible performance is a key issue in many applications which require in-depth investigation and understanding of
- The distribution, grafting frequency, uniformities and length/architecture of the grafted chains
- The influence of the synthetic factors on the characteristics of the grafts such as absorbed dose, dose rate, solvent, temperature, monomer concentration.
- The chemical composition, structural and morphological parameters and functional properties of grafted materials
- The covalent and non-covalent interactions between the grafts and the target species, especially for applications like sensors or catalysts.
- The thickness of the grafted layer, amount of functional groups on the graft chains, chain density in the grafted polymer zone.
- The structure, localization and spatial distribution of reactive intermediates
- The modeling or computational studies for elucidation of the aspects for a better understanding of the mechanism
- The mechanism and kinetics of the grafting process from different points, including monitoring of monomer consumption and formation of grafted copolymer, etc.
- The degrees of grafting especially in confined places such as the interior of a nanochannel to not block the entrance of the nanochannel
- The possibilities of applying controlled radical polymerization in conjunction with RIG techniques to overcome the drawbacks related to uniformity to some degree
- The accurate characterization of the structure and morphology of the grafted/surface modified material in detail using advanced experimental methods (AFM, ellipsometry, XPS, etc.)

f. The decrease of material loss and increase in performance in thin film technology strongly related to the following issues
Development of efficient methods that do not require surface post-treatments based on implantation technique for cutting thin layers from bulk material

- Increasing of the amount of the extended defects induced in the structure to a precise depth in order to create weakened zones.
- Optimization of detachment conditions according to both thickness and orientation of material
- Development of ion implantation protocols (fluence, energy) to produce nanostructures (nanoplatelets or nanocavities) in order to explore for detached ultra-thin substrates (Si, Ge, SiC) and to identify thermal annealing conditions (temperature, time).
- Investigations of the growth mechanism of extended defects.
- Accurate characterization of materials using advanced experimental methods such as DRX, SEM, PL, FTIR, TEM, UV-Vis, Surface roughness measurement, etc.

Magnetic thin films are used in electric devices such as planar inductor and transformer. By ion implantation, the material properties could be modified while preserving the crystal structures. The effects of ion implantation on the magnetic thin film related to the ferromagnetic resonance is a key issue which requires in-depth investigation of
- The location and the density of created defects
- Relationships between these defects and the magnetic properties
- Simulation tools for predicting the induced magnetic properties

Organic nanowires with single-type or segmented configurations can be fabricated from various organic molecules. With appropriate combinations of organic materials, the resulting nanowire arrays could potentially contribute in the fields of photovoltaic (energy) and light emitting diode (electronics), and in the production of superhydrophobic surfaces. To realize these benefits, the following key points must be investigated
- Method for producing orthogonally oriented nanowires
- Structure-function relationship of the synthesized nanowires

4.2.3. Molecular platforms, encapsulants and polymer blends
Fabrication methods, structure control, characterization, optimization, and interlaboratory reproducibility of the results in radiation synthesis of nanoparticles based on synthetic and natural polymers.

The inherent properties of the polymeric nanoparticles, e.g., interpolymer complex nanogels and amphiphilic polymer core shell nanoparticles, make them applicable as functional nanostructure template for entrapment and delivery of drugs, active compounds and pigments for healthcare, cosmeceuticals, agriculture and functional coatings. Nanoscale dimensions of particles increases the solubility of drugs and other active ingredients. Such nano-vehicles can efficiently stabilize and deliver the active ingredients to the desirable site.

In recent years significant progress has been made in radiation synthesis of polymer-based nanoparticles and nanogels, and advanced studies are underway to elaborate products for medical use based on these materials. Still, important questions remain regarding precise understanding of the underlying physical processes and chemical reactions, development of suitable fabrication methods, structure control, characterization, optimization, and interlaboratory reproducibility of the results in radiation synthesis.

Furthermore, many of these techniques and products are still based on the use of synthetic monomers or polymers. With the current general shift of paradigms in science and industry, we are inclined to seek for "greener" technologies and products which use biobased resources, e.g. substrates based on natural polymers. Polysaccharides are a natural choice, but the well-known problem of employing them in radiation processing is that nearly all of them predominantly degrade under the action of ionizing radiation, and thus they cannot be easily cross-linked. At the Partners’ labs several methods have been developed that allow for radiation-induced crosslinking of polysaccharides. In this CRP we undertake to elaborate new approaches which would allow for radiation synthesis of nanoparticles and nanolayers based on natural polymers. The products, having biocompatible and biodegradable properties, could serve as nanotechnology platforms for various products, for instance in the fields of environment protection, healthcare, agriculture as well as coating- and printing technologies.

The scientific gaps related to this topic include:
- Detailed understanding of the reactions and processes underlying the radiation synthesis of polymer nanoparticles

- Development of appropriate experimental techniques and protocols to study the formation as well as physical and chemical properties of the radiation-synthesized nanomaterials

- Understanding the kinetics and mechanism of radiation-induced inter- and intramolecular crosslinking of polysaccharides and the factors allowing to influence the crosslinking vs scission competition.

- Determining the factors influencing the formation and radiation crosslinking of H-bonded interpolymer complexes

- Validating the results by performing interlaboratory comparisons

**New tools for better understanding and precise control of radiation synthesis of polymer nanoparticles.** Rapid progress in nanotechnology is not quite fully matched with development of suitable research- and design tools. This is also true for radiation synthesis of nanomaterials. In the current CRP new experimental and simulation methods will be developed for deeper understanding of the chemical reactions and physical processes underlying radiation-assisted formation of polymer nanomaterials and for better and more efficient planning of such radiation syntheses.

**Scientific gaps:**

- Development, performance tests and optimization of the new system for pulse radiolysis with multiangle laser light scattering detection, allowing for time-resolved studies on radiation-induced reactions and processes in polymer systems

- Performing initial tests of the new system and first experiments on simple water-soluble polymer undergoing crosslinking and scission; developing ideas and algorithms for data processing and interpretation

- Application of the new pulse radiolysis system for studying intramolecular crosslinking as a process leading to the formation of nanogels
4.2.4. Nanostructured materials, dimensionally structured objects

One of the most important discoveries of chemistry and physics is the finding that the key properties of solids depend on the microstructure, i.e. (1) the unique combination of the chemical composition, (2) the size of a material in one, two or three dimensions, and (3) the arrangements of the atoms. If one or several of these parameters are altered, then the properties of a material would change too. Radiation processing is capable of modifying materials on a nanoscale level and as such can be used to produce materials with controlled microstructural characteristics. The application of radiation treatment techniques to modify dimensionally structured solids, e.g. graphene or other 2D materials, open new avenues in nanotechnology to engineer new properties and technological functions leading onto new device concepts and manufacturing methods. The list below summarises the key challenges in this area specific to this CRP.

Carbon based nanowires

Radiation technology offers unique capability to produce nanowires (< 10 nm in diameter) from organic materials. The Single Particle-Triggered Linear Polymerization (STLiP)” technique proposed here has a potential to become an important technology for fabrication of the nano-sized objects from π-conjugated small molecules. The following key scientific challenges are currently found in this area:

- Developing the chemistry allowing to remove structural defects and undesirable groups formed during SHI treatment in order to improve functional performance of a nanowire;
Replacing the inefficient post-irradiation solvent treatment procedure with sublimation or some other alternative technique.

2D carbon supported noble metal nanoparticles

In the field of heterogeneous catalysis, great attention is given to enhancing catalytic properties by the highly dispersed deposition of an active metal onto a support. As such, the development of an efficient preparation method to produce a highly dispersed active species on a support with a large specific surface is of particular importance. The following scientific challenges are identified for the “one pot” radiation synthesis of metal nanoparticle-2D carbon nanocomposites:

- Increasing understanding of a templating effect of 2D graphitic material in the radiation synthesis of supported metal NPs;
- Improving the knowledge of the mechanism of simultaneous radiation-induced reduction of metal ions and graphene oxide in different solvent media.

Control of morphology in hybrid materials

The radiation processing of hybrid materials (HMs) is an appealing alternative to the currently used sol-gel techniques as it creates new ways to produce advanced functional materials with unique properties, especially in instances when a traditional functionalisation isn’t straightforward. However, there is currently a substantial gap in the science underpinning the radiation induced production of hybrid materials; the key challenges being listed below:

- Improving the knowledge of the ionic liquid (IL)-assisted polymerisation using radiation processing;
- Developing the chemistry allowing to reduce the requirement for high doses currently used in hybrids’ fabrication;
- Enhancing understanding of the key parameters allowing to control porosity and surface morphology of a hybrid material in an easy and reproducible manner.

Radiation-driven Polymerisation-Induced Phase Separation (PIPS)

The PIPS is a convenient tool to control the morphology of polymer blends, for multiple applications in membrane technology, surface patterning, thermoelectrics and solid-state lighting,
etc. However, to put the radiation-driven PIPS on a solid scientific footing, the following issues need to be addressed:

- Improving understanding of the polymerisation kinetics, dependent on the dose rate, blend’s composition and other physical parameters (e.g. temperature) to better control phase separation process;
- Achieving better knowledge of a nanocomposite’s morphology and mechanical properties at break;
- Establishing the key “structure-properties” relationships for the rational design of blends.

**Radiation-induced modification 3D-printed thermoplastic objects**

Additive manufacturing (or 3D printing) is ideal for creating objects of complex geometry rapidly and economically. 3D printing is well suited for testing ideas, building bespoke devices and trying new designs with limitless applications in mechanical engineering, fabrication of medical devices and prostheses, and production of advanced research equipment. Combining the additive manufacturing with radiation processing will lead to the development of printing of entirely new functionalised polymers and polymer composites. Resolving the following scientific challenges is needed in this area:

- Improving understanding of the compatibility of thermoplastic materials with the desired behavior, e.g. (1) what additives can be used when crosslinking is required; (2) selection of initial MW for the base polymeric material; (3) in biomedical applications: biocompatibility issue.
- Developing the underpinning science and associated preparation protocols for 3D- and 4D-printing of thermoplastics with nanofillers for: (1) efficient dispersion of a nanofiller in a matrix; (2) fabrication of modified nanofillers; (3) specifications for the blending equipment; (4) precise control of the distribution and orientation of the anisotropic nanofillers (e.g. CNC);
- Establishing the key “structure–properties” relationships.

**Post-printing radiation modification of 3D hydrogel structures**

Hydrogels possess unique properties such as flexibility, softness and high-water retention. The resemblance of hydrogels to living tissues opens up many opportunities for applications in the
biomedical area. Polymer hydrogels can be both synthesized and modified by radiation, e.g. a hydrogel can be decorated with metal NPs using in-situ by radiolytic reduction. The following fundamental science underpinning is required in this area:

- Improving understanding of the influence of swelling on initial dimensions and mechanical integrity of the parent structure;
- Developing chemical approaches mitigating degradative impact of radiation on the base polymer (e.g. polysaccharides or PHEMA);
- Enhancing the efficiency of the radiolytic synthesis of metal NPs within the hydrogels;
- Developing robust copolymer systems which exhibit the lower critical solution temperature behavior;
- Establishing critical “structure-properties” relationships.

**Graphene-based anticorrosion coatings**

Graphene is a popular nanofiller used for fabrication of polymer composites with improved mechanical and functional properties. In particular, polymer films containing graphene or reduced graphene oxide nanoflakes are deployable for the protection of metals against corrosion. However, the following scientific gaps need to be filled to enable the development of graphene-based technology:

- Developing scientific background for a cost-effective way of producing exfoliated graphene in large quantities;
- Overcoming the issue of graphene nanoflakes polydispersity allowing to produce higher quality composite coatings.

**4.3. TECHNOLOGICAL CHALLENGES BY DOMAIN OF APPLICATION**

The research activities proposed for this CRP project include technological challenges on specific application-oriented targets that will guide the development of generic synthetic methods and provide the opportunity to benchmark the performances of the developed nanoproducts. This includes Environment Environmental application (i.e. radionuclides, pollutants, sensors for pollutants, catalysts for depollution), Electronics and energy (silicon materials, photothermal),
Medicine, Healthcare, Cosmetics, Chemical industry, catalysis, Advanced Functional Materials (composites, packaging, cultural heritage, coatings, materials with specific properties), Food and Agriculture (antibacterials for aquaculture). In the following, the technological challenge of each of them are explained and itemized. The complete working document is available in ANNEX II.

4.3.1. Environment

Environmental Protection, Control and Remediation can benefit from the recent advances in nanotechnologies and nanomaterials. The current limitations identified during the meeting relate to lack of sensitivity, robustness, integrability and cost-efficiency. Effective solutions for water purification, sensing and removal of pollutants need to be cost-effective, competitive and scalable.

In this field of application, the main technological challenges to be addressed as follows:

- Requirement of compatibility of developed sensors with existing analytical equipment
- Need for production of stable and cost-efficient membrane catalysts and titania-based photocatalysts for removing of organic dyes from water sources
- Solving the issue of stability and cost-efficiency for radiation-produced hybrid materials based on green technological approach
- Developing advanced ion beam source capable of producing higher pore density for filter membrane production and scaling up the related production technology.

4.3.2. Electronics and energy

In the electronics and energy fields, possible technological challenges are mainly classified in two issues—materials and interfaces, both of which are related to the control of their nanostructures through radiation processing. Through these challenges, two outputs will be expected. One is the development of less expensive alternatives to the currently used materials. The other challenge is the development of new materials or methodology to access them, which has not yet been addressed so far. Durability and scalability are also the important factors for practical industrial applications.

In this field of application, the main technological challenge to be addressed are as follows:
- Development of advanced assembling process to obtain nanoscale p-n heterojunctions from organic nanowires for photon-energy conversion devices and production of carbon-based nanowires with sufficient electrical/thermal conductivities
- Enhancing the performance of stimuli-responsive hydrogel materials and devices for industrial applications
- Design of nanostructure synthesis systems and development of scalable printing techniques and protocols ready to be used as conductive inks for the fabrication of RFID/NFC tags
- Substituting noble metallic nanoparticles for fuel cells/supercapitors/batteries with less expensive transition metal NPs.
- Developing competitive, scalable, durable, commercially viable fabrication techniques for the electrochemical energy device
- Developing of new highly efficient and inexpensive thin films of Si for photovoltaics applications

4.3.3. Medicine, Healthcare, Cosmetics

In this vital field of application, the fabrication of nanomaterial-based products for medical treatment, healthcare products and cosmeceuticals must be developed and scaled guided by biocompatibility, non-toxicity and preferable use of natural materials.

*In this field of application, the main technological challenge to be addressed are as follows:*

- Need for development of the methods for fabrication of new hydride-type nanocarriers to be used as selective radiosensitizers in cancer therapy
- Need for development of periodontal splint combining the valuable properties such as good biocompatibility, easiness to use and replace, stability, aesthetic appeal and cost-efficiency.
- Developing hybrid materials with controlled and reproducible bioactivity, porosity and surface morphology for successful bone consolidation
- Need for production of stable and cost-efficient antimicrobial coatings for every-day applications
- Requirement for substitution of synthetic polymers with bio-based materials and development of mild synthesis and processing conditions to obtain nanomaterials for medical, healthcare, cosmeceutical purposes.
- Designing of simple and scalable manufacturing processes for industrial transfer in this domain, taking into account health and safety issues

4.3.4. Chemical industry, catalysis

In this field of application, it is important to develop new approach for fabrication of nanoparticle-based catalysts featuring high catalytic activity, high stability, reusability and cost-efficiency.

In this field of application, the main technological challenges to be addressed are as follows:

- Need for development of new cost-efficient hybrid-type film, templated and composite porous catalysts for synthetic chemistry or electrochemical processes.
- Replacing of noble metals with less expensive transition metals in industrial catalysts
- Promoting radiation processing technique for the mass production of nanostructured catalysts

4.3.5. Advanced Functional Materials

Within this application domain, multiple areas for development have been identified, including: composites, packaging, cultural heritage, coatings, materials with specific properties.

In these fields of application, the main technological challenges to be addressed are as follows:

- Need for development of new cost-efficient methods for production of soft hybrid metal-polymer materials and porous composites with specific magnetic and optical properties for applications in electronics and photonics.
- Need for new approaches for manufacturing superhydrophobic surfaces modified with nanowires
- Developing of suitable and potentially scalable manufacturing technologies for the production of effective active (nano)composite polymeric materials
- Exploiting ferromagnetic properties of heterogeneous (solid) catalysts in the transesterification process to remove them from reaction mixture.
- Optimizing the radiation-induced production of hybrid materials in ionic liquids to satisfy cost-efficiency, scalability and biocide activity requirements.
- Developing of new anticorrosion coatings based on graphene composites produced by radiation chemical technique.
- Optimizing nanostructure synthesis and system design for coating/printing techniques that can be simplified and scaled-up for industrial transfer
- Preparing manufacturing protocols of nanoparticle use in this domain

4.3.6. Food and agriculture

In this field of application, it is important to develop new approach for fabrication of nano-fertilizers or nano-encapsulated nutrients that can be applied for minimizing nutrient, minimizing the loss of fertilizer and increasing crop yield. Another important goal is to produce active nanoparticles and nanocomposite films for shelf-life extension of packaged food products.

In this field of application, the main technological challenge to be addressed are as follows:

- Requirement for substitution of synthetic polymers with bio-based materials and development of green technologies to obtain nanomaterials for plant growth, crop production, extending food self-life.
- Optimizing nanostructure synthesis and protocol, techniques and manufacturing process that can be simplified and scaled-up for industrial transfer in food, agricultural and aquaculture applications
- Addressing the environmental effect of nanomaterials in soil and irrigation system and the safety issues related to cytotoxicity and eventual migration of radiolytic products from irradiated (nano)composite polymeric films

4.4. INSTRUMENTAL NEEDS AND RECENT DEVELOPMENTS IN RADIATION TOOLS
Available equipments

Instrumental needs for conducting ambitious research in the field of nanoscience and nanotechnology encompass easy access to adapted irradiation facilities and availability of equipment for the fine characterization of nanomaterials and nanostructured materials.

The inventory of radiation sources and equipment in operation at the institutions of the participants cover practically all the current needs in terms of:

- Spectroscopic methods (UV-vis, FTIR, Raman, (beta)NMR, photoluminescence, XPS, ESR),
- Mass spectrometry (MS-MS, Q-ToF, MALDI, SJMS),
- Scattering methods (DLS, SLS, SANS),
- Diffraction methods (SAXS, WASXS, 4-circle XRD),
- Imaging (SEM, TEM, EDX, AFM, micro-PIXE, STIM (ion microscopy))
- Chromatography (SEC, HPLC),
- Surface properties (Zeta potential, contact angle measurements),
- Morphological characterization (BET, X-ray tomography, PALS),
- Mechanical and thermophysical properties (DSC, DMA, TGA, mechanical tests),
- Rheometry and viscometry,
- Bioassays (MTT, … specific interactions, in vitro, in vivo),
- Miscellaneous techniques in relation with the desired functionalities (permeation, voltammetry).

The detailed list of equipment and facilities is available in ANNEX III.

A limited number of institutions or laboratories are equipped with specific analytical methods such as time-resolved spectroscopy for studying fast dynamic processes following irradiation of solutions and materials. Collaborative projects in this field will allow the participants to share
their resources for deepening the basic knowledge and establishing new structure-reactivity and structure-properties relations with significant impact on the development of the nanotechnologies.

**Recent instrumental developments and future needs**

The use of the radiation technology plays an important role in the production and investigation of nanomaterials. Available radiation sources such as high-energy charged particles (electrons and ions), x rays and gamma rays are widely used in nanoparticles, grafted and surface modified materials, molecular platforms, encapsulants and nanostructured materials. One of basic research and industrial application of radiation methods in the nanotechnology is the used of swift heavy ion beams to modify various materials. There are large ion beam facilities such as FLNR (Russia), GANIL (France), BNL (USA), GSI (Germany), TIARA (Japan) and INPRK (Kazakhstan) which have been running successively for polymer membrane researches. However, they are expensive to construct and maintain, and also provide short beam service times.

In order to be compact in size and easy in operation and maintenance, a Radio-Frequency Quadrupole (RFQ) based ion accelerator is proposed at Korea Atomic Multipurpose Accelerator Complex (KOMAC). It mainly consists of an electron beam ion source (Ar, Kr, Xe ions), a RFQ accelerating cavity (1 MeV/n), a beam transport system and a membrane-irradiation chamber. The electron beam ion source and the RFQ at KOMAC are under manufacturing. The RFQ based ion accelerator is initially expected to produce swift heavy ion beams of Kr and Xe ions of 1 MeV/n respectively. With a careful design of ion beam optics and irradiation chamber, an irradiation system of uniform 2D beam profile and position-controllable ion beam will be provided for nanostructured membrane formation.

4.5. **FORESEEN COLLABORATIVE ACTIVITIES**

The 1st RCM has been particularly successful also in the identification of possible cooperation activities among the partner institutions. Due to the complementarity of competences and of the available facilities and instruments highlighted during the meeting, productive research activities
on specific topics addressed in the frame of the CRP will be jointly conducted. After fruitful discussion, participants have built the Interaction table presented below.

In the matrix, the yellow boxes identify the collaboration between the partners (given by the row-column intersection). In each yellow box, the topic of the potential collaboration is indicated and is coded with a letter and a number which represent, the Domains of application and the identified class of nanomaterial introduced in section 4.1.

Domains of application:
A) Environmental Application
B) Electronics and Energy
C) Medicine, Healthcare, Cosmetics
(D) Chemical Industry, Catalysis
(E) Advanced Functional Materials
(F) Food And Agriculture

Class of nanomaterial
1) Metal Nanoparticles
2) Grafted And Surface-Modified Materials
3) Molecular Platforms, Encapsulants, Blends
4) Nanostructured Materials Dimensionally Structured Objects

Table summarizing the foreseen the collaboration between 2 or more partner laboratories.
Metal nanoparticles constitute one of the major current materials in nanotechnology, with many products already on the market and strong perspectives for further growth. It is also known since some time that metal nanoparticles can be synthesized using ionizing radiation and that this method has some important advantages over the typical chemical ones, the main one being the absence of chemical reducing agents. However, there are also some not yet fully understood factors which may influence the outcome of radiation syntheses, including product properties and stability. This may also cause reproducibility problems and makes it difficult to compare results obtained at different laboratories. It may also discourage research labs and industry from applying the method.

At IAEA there is a body of experience indicating that such problems can be tackled by performing well-planned interlaboratory studies. Since among the candidate participants of this CRP there are a number of labs having some experience and/or interest in radiation synthesis of metal nanoparticles, the accumulated knowledge and experience can be used in preparing a good plan.
for such a study, identifying the critical factors, establishing ways of dealing with potential problems and finally for running an interlaboratory study on one or more products. Such a study may not only lead to an increase in experience, skills and self-confidence of the participating laboratories, but also, in future, in greater confidence in the reliability and reproducibility of the radiation technique for the synthesis of metal nanoparticles.

The topic of the exercise is performing, at every participating laboratory, a radiation synthesis of metal nanoparticles, under controlled conditions and according to a precise protocol, as well as determination of the properties and stability of the products by pre-selected methods according to procedures agreed upon.

The aim of this interlaboratory exercise is to identify suitable, well-controllable conditions and a reliable procedure for radiation synthesis of metal nanoparticles, check the reproducibility and robustness of this procedure when tested at various labs and identify potential factors influencing the outcome of this process. A more general aim is to increase the experience, skills and self-confidence of the participating laboratories in performing radiation-based material syntheses.

The following participants expressed their interest in participating: Brazil, Egypt, France, Poland, Russia, Thailand and UK. The list is open.

General action plan for the exercise is the following:

- Collecting information from the participants regarding existing facilities (gamma, EB, dose rates, analytical equipment, preferences)
- Analyzing the existing knowledge
- Selecting and agreeing upon the basic issues such as analytical techniques and protocols, places where particular analyses would be performed (on site or/and at a designated lab)
- Elaborating, testing and optimizing the standard protocol for the synthesis of metal nanoparticles and indications as to the preferred analytical procedures (by selected lab(s))
- Consulting the protocol with all participants, approval of the protocol
- Procurement and distribution of chemicals
- Performing the synthesis by the participating labs
- Analyzing the products (on site and/or after sending them to other designated lab(s))
- Sending over reports to the coordinating labs
- Data analysis; elaboration of the common report, comparison of the results obtained at various labs.
- Identification of problems (if any), modification of the protocol
- Reiteration of the exercise, if necessary
- Final data analysis, preparation of the final report

5. CONCLUSION

The participants concluded that the technical meeting was very successful in providing dense technical and scientific information on their background activities and on their specific contribution to the CRP.

The objectives of the proposed workplans were analyzed and discussed to identify the common and the features of the research programmes. This resulted in matrix representation based on the class of materials that was central to each project and on the domain of application foreseen.

In the perspective of the short-term transfer to industry of the achievements of the program, the main drivers for the research and development activities were discussed for 6 main fields of application, covering Environment, Electronics and Energy, Healthcare, Functional materials, Chemical Industry, Food and Agriculture (noted A to F).

Four classes of materials, noted 1 to 4, were considered: Metal nanoparticles, Grafted or surface-modified materials, Molecular platforms, encapsulants and polymer blends, nanostructured materials and dimensionally structured objects.
To benefit from the added value brought by collaborative interactions between participants having complementary expertise, thorough discussions were held on cooperative and networking activities among the participating laboratories. More than 30 bilateral or multi-partner collaborations were identified of topics of common interest.

The CRP, due to its broad front of concerted actions in various domains of radiation processing and nanotechnology, is expected to yield documented achievements covering the following aspects:

- Deeper knowledge and better understanding of the physical and chemical phenomena underlying the radiation-driven nanofabrication processes and product properties;

- Advanced simulation and experimental techniques for the rational design of alternative synthetic approaches and for new nanomaterials;

- Novel value-added products based on nanomaterials with enhanced performance for Environmental Protection and Remediation, Electronics and Energy, Chemical Industry, Advanced Functional Materials, Food and Agriculture, Healthcare and Medicine, as well as nanofabrication methodologies employing ionizing radiation;

- Uniform protocols validated by interlaboratory studies for synthesizing and testing selected nanomaterials by radiation techniques.
6. RECOMMENDATIONS

CRP partners should address the scientific gaps regarding the most urging topics in the field of radiation-synthesized nanomaterials and to endeavor to fill the scientific gaps between the current state of the art and the emerging needs in application of radiation technology in nanomaterials and nanoprocessing. In particular, it is recommended to address the following issues:

1. Control of the key processing parameters. To achieve this goal, it is important to develop better understanding and better control of the physical processes and chemical reactions underlying the radiation synthesis of nanomaterials in two principal aspects;

   - Elaboration of new approaches to control the radiation-induced formation of nanostructures and manipulate their structure, localization and distribution using various radiation types (gamma-rays, e-beams, ion-beams, X-rays) and adjusting the radiation parameters;

   - Investigation of the key chemical aspects for controlled synthesis and modification of nanostructured materials on the basis of improving understanding of the kinetics and mechanism of various radiation-induced chemical processes (metal ion and graphene oxide reduction, assembling of NPs, grafting, crosslinking, modification)

2. Control of morphological parameters. It is important to develop the approaches to optimize the architecture of nanomaterials of different shape and dimensionality by controlling the nanostructure pattern at all the stages of their fabrication (starting from optimization of templates to post-irradiation treatment)

3. Methodological aspects. It is necessary to develop new methodologies and tools, both experimental and based on simulations, allowing to gain more insight in the synthetic and structural aspects of radiation formation of nanomaterials and to provide guidance in planning the syntheses and design of the products. It is also very important to combine the unique features of nanomaterials with the dimensionality of the objects made thereof.

4. Exploring the potentialities of biobased resources, including natural polymers, for the synthesis of nanomaterials
5. Performance is a key benchmark for successful commercialization of the developed innovation. Application-oriented activities conducted in the frame of this CRP should aim at efficient, robust and durable materials or systems.

6. To guarantee public acceptance and sustainability of the proposed innovations, participants are committed to minimize the environmental footprint of their technological approach. In this respect, radiation processing offers significant advantages for developing green technologies.

7. To facilitate the transfer of research innovations to industry, it is recommended that participants design synthetic pathways and define fabrication processes allowing for easy scalability and good integrability with existing technologies, and at competitive costs.

8. To disseminate the results of their research, the participants are recommended to use IAEA publications and peer-reviewed journals with high impact factor.

9. It is recommended that IAEA organizes the 2nd RCM either in Egypt, France or Portugal during the last quarter of 2020. The proposed dates for the one-week meeting would be from September 21-25 or October 5-9, 2020.
ANNEX I - COUNTRY TECHNICAL REPORTS

BRAZIL

SUSTAINABLE SYNTHESIS OF METAL/METAL OXIDE /GRAPHENE BASED NANOCOMPOSITES FOR RENEWABLE ENERGY SOURCES AND STORAGE

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Abstract
The traditional chemical methods to produce metal/graphene based nanocomposites do not yield high quality nanomaterials, presenting undesirable heterogeneities in size and shape. In addition, the process usually involves toxic reagents that contaminate the final nanocomposites decreasing the quality of the electrode and catalysts.

The main objective of this project is to incorporate metal/metal oxide/ graphene based composite using the ionizing radiation technique to produce catalysts and electrodes with high purity using water or water/alcohol as solvent in scalable synthesis. The final product will be used in supercapacitor, PROX-CO process and fuel cells devices.

1.INTRODUCTION

Carbon materials have been widely used in both analytical and industrial electrochemistry. Most recently, inorganic/Graphene-based nanocomposites have attracted attention due to their peculiarities in combining properties for many applications, such as for energy storage, electrochemical devices, fuel cell technology, catalysis, sensing and photonics [1].

Traditional chemical reduction for the incorporation of metal nanoparticle on graphene based nanomaterials involves toxic reagents, it is a time-consuming method and it also requires high costs for the removal of excess reagents and by-products. In addition, trace amount of these highly toxic reagents remains on the sheet surface after reduction process, decreasing the performance of the nanocomposites. A new method to produced metallic nanoparticles on GO surface is using
electron beam irradiation (EB) [2-3]. The EB is paid more attention because of green, fast and mass production with low cost [2].

Herein, we demonstrated a green and efficient one-step method based on electron beam (EB) radiation to produce Pd/rGO nanocomposite.

2.MATERIALS AND METHODS

2.1. REAGENTS

Graphite (powder puriss, CAS: 7782-42-5) was acquired from Merck. Sodium hydroxide (NaOH), 98% sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), 30% hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), and 37% hydrochloric acid (HCl) and Pd (NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O of analytical grade were acquired from Sigma Aldrich. Solvents were purified by standard procedures. Deionized (DI) water was used in all experiments.

2.2. SYNTHESIS

2.2.1. Graphene Oxide (GO) was prepared according to the modified Hummers method. [4]

2.2.2 rGO was prepared using thermal reduction method [5].

2.2.3. Pd/rGO nanocomposite were synthesized using electron beam method. Palladium salt solution [Pd (NO\textsubscript{3})\textsubscript{2}] was dropped into exfoliated rGO solution (1.5g/L water/isopropanol (1:1) by magnetic stirring under nitrogen atmosphere for 5 min. After that, the solution was irradiated with electron beam using electron accelerator Dynamitron 37.5 kW (E = 1.5 MeV, 25 mA) by Radiation Dynamics Inc. Finally, the obtained black product, Pd/rGO, was washed using DI water and vacuum dried at 50 °C for 24 h.

2.3. CHARACTERIZATION TECHNIQUES

Pd/rGO was characterized through Thermogravimetry (TG, TA Instruments SDT-Q600), X-ray diffraction (XRD, Bruker, D8 advance) and Raman spectroscopy (Renishaw in Via Reflex). TG was performed using alumina, heat flow 20 °C.min\textsuperscript{-1} until 800 °C under dynamic air atmosphere of 100 mL. XRD were obtained using copper tube, from 2° to 70° 0. Cyclic voltammetry (CV) was used to investigate the electrochemical behaviors of the Pd/rGO. CV studies were conducted at Potentiostat (μAutoLabIII/Fra2- Metrohm Autolab) on scan rate of 10 mVs\textsuperscript{-1} in KOH (0.1 mol.L\textsuperscript{-1}) first in absence, then in presence of ethanol (P.A.). The experiments were carried out with
nitrogen saturated solutions of 1 M CH₃CH₂OH in 1 M KOH, within a potential range of -0.85 to 0.2 V (vs. Ag/AgCl).

3. RESULTS

Firstly, Pd²⁺ ion was easily coordinated with negatively charged oxygen-containing functional groups on GO, followed by EB irradiation leading to Pd nanoparticles formation on GO surface. The synthetic routes for the preparation of Pd/rGO nanocomposites are summarized in figure 1.

![Synthetic route for Pd/rGO](image)

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**FIG 1-Synthetic route for Pd/rGO**

X-ray diffraction (XRD) analysis was done to determine the crystalline structure of the Pd nanoparticles supported on rGO surface. These analyses showed three peaks at 40.1°, 46.6° and 68.0°, which could be assigned to the (111), (200) and (220) crystalline planes of the face centered cubic (fcc) structure of the Pd lattice, indicating successful formation of palladium nanoparticles on rGO sheets through the incorporation by electron beam as shown in Figure 2.

![X-Ray diffraction patterns for Pd/rGO and rGO](image)

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**FIG 2- X-Ray diffraction patterns for Pd/rGO and rGO**
In addition, the diameter of Pd nanoparticles produced was determined as 3.0 nm. The amount of incorporated Pd (20% w) was determined by thermogravimetry (TG) (Fig.3).

![Graph showing weight percentage vs. temperature for rGO and Pd/rGO.](image)

**FIG 3- X-Ray diffraction patterns for Pd/rGO and rGO**

The Figure 4 shows cyclic voltammetry of (a) rGO and (b) Pd/rGO as electrode. There is no significant current observed for the rGO for the alcohol oxidation, which is justified by the absence of Pd. For Pd/rGO electrode, two alcohol oxidation peaks can be clearly observed in the cyclic voltammograms.

![Cyclic voltammograms of rGO and Pd/rGO irradiated with 288 kGy in nitrogen saturated solution of 1M KOH containing 1M CH3CH2OH at a scan rate of 50 mV.s⁻¹.](image)

**FIG 4-Cyclic voltammograms of rGO and Pd/rGO irradiated with 288 kGy in nitrogen saturated solution of 1M KOH containing 1M CH3CH2OH at a scan rate of 50 mV.s⁻¹.**
The forward scan of the CV curves is characterized by a strong current peak at about 0.1 V for the ethanol oxidation. The reverse anodic peak at -0.1V is primarily a result of the removal of the incompletely oxidized carbonaceous species formed during the forward scan. The mass activity of the ethanol oxidation in 1 mol.dm$^{-3}$ ethanol solution on Pd/rGO was 133 mA mg.Pd$^{-1}$.

4. CONCLUSION

Pd/rGO and nanocomposite was prepared by a rapid, eco-friendly, one-step EB based method, without using any reducing agent. Pd/rGO was used as catalyst to electrochemical ethanol oxidation, which can be used as advanced electrochemical or chemical materials.

5. REFERENCES


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RADIATION SYNTHESIS OF GRAPHENE NANOCOMPOSITES AND THEIR APPLICATION FOR METAL CORROSION PROTECTION

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Abstract

Green and large scale method for preparation of GIG nanosheets from pre-exfoliated GO was achieved. The reduction process was conducted using gamma radiation. Isopropanol was added to induce the reduction of GO during the irradiation processes and transform oxidative \( \cdot \text{OH} \) radicals into reductive alcoholic radicals. The presence of capping agent as CMC is important for the completion of reduction process via gamma radiation and also for stabilization of obtained GR nanosheets. The resulting graphene was characterized using UV-Vis, XRD and FE-SEM. The extent of corrosion protection of stainless steel by gamma ray induced graphene (GIG) and its composite with chitosan (GIG/CS) and organic inhibitor GIG/Inhb. in 3.5%NaCl and 0.5M \( \text{H}_2\text{SO}_4 \) solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy measurements. The protection efficiencies calculated from potentiodynamic polarization for GIG and GIG/CS in in 3.5%NaCl were 82.2% and 89%, respectively. Meanwhile, the protection efficiencies for GIG and RG/Inhb. in 0.5M \( \text{H}_2\text{SO}_4 \) were 76 % and 95 %, respectively. The effect of temperature on the coatings performance was investigated. GIG/CS and GIG/Inhb film over steel showed higher corrosion activation energy compared to GIG. Impedance measurements proved the stability of GIG and GIG/CS coatings after different immersion times in 3.5%NaCl and 0.5M \( \text{H}_2\text{SO}_4 \) solutions.

Keywords: Graphene; Corrosion inhibition; Polymer composite; Gamma irradiation.

1. INTRODUCTION

The most widely used definition of corrosion is the degradation of material by its reaction with its environment. Corrosion results in severe costs for the society. The impact of these costs can be economical, environmental, or on human safety. Corrosion is a serious problem because it can lead to plant shutdowns, product contamination, loss of valuable parts and costly repairs associated with production losses. In addition, corrosion has its impact on the safety of the environment. Protection of metals from corrosion is a vital issue in different fields and many industries. The development of new corrosion protection techniques has attracted substantial interests. The interest in corrosion science arises from its costly damages. So far, many corrosion prevention techniques
have been established their applications in marine, pipeline, aerospace, automobiles, construction industries and so forth. However, demand for new and robust techniques of high corrosion protection efficiency still a challenging issue to increase the life cycle of natural resources for economical savings. The major principles for corrosion prevention are the modification of the environment, modification of the materials properties, application of protective coatings, or cathodic and anodic protection [1-3]. Materials are protected from corrosion through a wide variety of methods. The main concept for corrosion protection is to remove one or more of the corrosion cell components. Another approach for corrosion protection is the change of the nature of the anode to become the cathode. The importance of coating cannot be emphasized because it combines all the corrosion control and prevention techniques such as barrier effects, inhibition (modification of environment), sacrificial effect (cathodic protection), and development of corrosion resistant materials such as conducting polymers (materials selection) [4]. Coating materials are classified into metallic, inorganic and organic. The application of a coating on the surfaces to be protected acts through one of the following main three mechanisms or by combination of them: Barrier effect, which prevent the contact between substrate materials to be protected and its environments. ii) Cathodic protection, where the coat acts as a sacrificial material. iii) Inhibition, which includes anodic protection [5]. Recently, one of the newest approaches is what is called “activepassive” which combines the barrier action of the coating material and the active approach through the formation of effective passive layer and this will inhibit the corrosion half reactions leading to Schottky barrier at the interface resulting in depletion of electrons [6]. Composite materials have a wide range of properties to be conferred on the coating materials, which improve the corrosion protection efficiency. Among these properties; good adhesion characteristics, strain tolerance, self-healing characteristics, heat conductivity There are other factors encourage the use of hybrid materials such as environmental, economic, technical and social factors. The aim of the present work is to use gamma irradiation as a safe and useful route to reduce graphene oxide to graphene and also to evaluate the prepared Graphene and its composites with an effective coating against corrosion of metals in 3.5% sodium chloride or 0.5M H₂SO₄ electrolyte.
2. EXPERIMENTAL

2.1. PREPARATION OF GAMMA IRRADIATED GRAPHENE (GIG) AND (GIG/CS) MIXTURE

Graphene oxide (GO) was first prepared from graphite powder according to Hummers’ method [7]. Thus, 1 g of graphite powder was added to 70 ml of concentrated H$_2$SO$_4$ at 0°C. 0.5 g of sodium nitrate was slowly added to the mixture and vigorously stirred in an ice bath and 4.0 g of potassium permanganate was added to the suspension. The ice-bath was then removed, and the temperature of the suspension is brought to 35°C with stirring for 2 hours, then 50 mL of water was slowly added. The brown suspension was maintained at 98°C for 15 minutes. The suspension was then further diluted with approximately 160 mL of water and treated with 30% hydrogen peroxide. The suspension turned into bright yellow color. Graphene oxide was then filtrated and washed several times with 5% HCl and water and left to dry.

Gamma irradiated graphene (GIG) was prepared by radiation induced reduction of GO. Thus, GO was dispersed in isopropanol/water (0.5 v/v %) mixture to obtain a final concentration of 1 mg/ mL GO dispersion. The as-prepared dispersion was sealed and exposed to $^{60}$Co γ-ray source under the condition of an absorbed dose 50 kGy with 2.5 kGy/h dose rate at room temperature. After the irradiation, the solution color was converted into black indicating the complete reduction of GO. The sample was washed with ethanol and distilled water and the irradiated graphene was left to dry. GIG suspension was obtained by dissolving 1.5 mg graphene in 1 mL DMF.

To obtain GIG/CS mixture, a 0.5% (mass ratio) chitosan solution was prepared by dissolving chitosan in 1.0% acetic acid solution then 10 μL of CS solution was added to the above GIG suspension.

2.2. ELECTROCHEMICAL CELLS AND EQUIPMENTS

The cell used for electrochemical measurements was a typical three-electrode/five-compartment glass cell. The working electrode was a 316 stainless steel alloy, reference electrode...
was Ag/AgCl (4.0 M KCl) and a Pt wire (5 cm long; diameter: 2 mm) as auxiliary electrode. Electrochemical impedance spectroscopy measurements (EIS) were employed to monitor the corrosion performance of the coated 316 stainless steel substrates in a 3.5% NaCl solution. EIS measurements were carried out at the open circuit potential (OCP), using a Gamry-750 instrument and a lock-in-amplifier that are connected to a personal computer. The data analysis was provided with the instrument and applied non-linear least square fitting with Levenberg-Marquardt algorithm. All impedance experiments were recorded between 0.1 Hz and 100 kHz with an excitation signal of 10 mV amplitude.

The potentiodynamic polarization test was used to determine the overall corrosion behavior of the specimen. The potential of the electrode was swept at a rate of 1 mV/s from the initial potential of -250 mV versus open circuit potential (OCP) to the final potential of +250 mV versus OCP. Before the test, the electrode was left under open-circuit conditions until a steady corrosion potential value was reached.

3. RESULTS AND DISCUSSION

3.1. PREPARATION OF GRAPHENE FROM GRAPHENE OXIDE

The effect of γ-ray irradiation on the reduction of GO sheets and the mechanism of radiation induced reduction of GO in the presence of isopropanol /water system was investigation. On the basis of the established principles of radiation chemistry, reductive radicals can be deemed as the real reductant for GO reduction, which is produced from water and alcohol molecules under γ-ray irradiation. High energy irradiation may induce radiolysis of molecules and the formation of highly reactive free radicals. γ-ray irradiation can decompose water molecules to both reductive (hydrogen radical and hydrated electron, \( ^\cdot \text{H} \) and \( e^{-}_{\text{aq}} \)) and oxidative (hydroxyl radical, \( ^\cdot \text{OH} \)) species, as shown in equation (1) in scheme (1) [8]. Alcohols are employed to remove the oxidative \( ^\cdot \text{OH} \) radicals as radical scavengers and transform oxidative radicals into reductive alcohol radicals in order to create a reducing medium as indicated in equation (2) [9]. In this study, isopropanol [(\( \text{CH}_3 \)\(_2\)\text{CHOH} \)] was employed. The reactions of \( ^\cdot \text{H} \) and \( ^\cdot \text{OH} \) radicals with isopropanol occur mainly at the α-carbon position, and produce reductive radicals as in equation (3, 4).
When GO sample, was dissolved in water without addition of isopropanol, and exposed to $\gamma$-irradiation, the reduction of oxygen containing functional groups did not occur and the sample retained its brown color after exposure to radiation. This result indicates that isopropanol addition is very necessary to induce the reduction of GO during the irradiation process. Compared to other alcohols, isopropanol produces high yield of reductive radicals causing elevated reduction level of GO. Isopropanol’s radical ((CH$_3$)$_2$·CH(OH)) exhibits mediating reactivity and steric size and provides sufficient diffusion time to approach GO sheets [10]. It is also found that the reduction degree of GO in inert atmosphere is higher than that in air because oxygen is a powerful scavenger for hydrated electrons and hydrogen radicals and encourages the generation of strong oxidative species, including H$_2$O$_2$ and O$_2$ [11]. The first ionization energy of N$_2$, O$_2$ and H$_2$ are 1402.3, 1313.9 and 1312 kJ mol$^{-1}$ respectively. Hence, the oxygen rich environment slightly leads to increased content of the oxygen rich groups across the surface of GO sheets.

On the other hand, the presence of hydrogen, with its lower ionization energy required to form hydrogen radicals, results in clear reduction of oxygen rich sites across the GO sheets giving a higher degree of re-graphitization without noticeable increase of morphological defects [12]. The relative molar concentrations of these gases in air with these differences in their ionization energies may have significant effect on the reduction efficiency. In other words, isopropanol-addition and oxygen-free medium are essential factors during $\gamma$-irradiation process in order to assure the reduction of oxygen-containing functional groups in GO. The radicals’ reactions are considered as diffusion-controlled reactions due to their high chemical reactivity [13]. Hence, the good dispersion of reactants in a system is very critical to increase the reaction efficiency. GO is poorly soluble in alcohols compared with water [14]. Therefore, a very low ratio of isopropanol was added
to water as the excess isopropanol results in lower dispersion of the GO in the solvent mixture and decreases the probability of reductive radical contact with GO sheets, which knocked down the reduction effect. The degree of reduction is homogeneous across the thickness of the 3D architecture and can therefore be tuned by adjusting the total irradiation dose and dose rate. In this study, a medium exposure dose (50 K Gy) was used to achieve the reduction of GO. It is easy to understand that increasing absorbed dose is important to increase the reduction efficiency via producing more radiolysis species, reductive radicals and hydrated electrons that are the main reason for GO reduction by irradiation.

However, using an extremely high dose decreases the reduction efficiency and could destroy the valence bonds of the graphite layer causing its reaction with other molecules [15]. The reduction efficiency is also affected by the radiation dose rate. The low dose rate (in this case 2.5 kGy h⁻¹) leads to a higher reduction level, while the high dose rate causes a lower reduction level. This could be attributed to the overly fast local reaction with GO in case of the high dose rate, which in turn increases the GO aggregation and hinders the diffusion of radicals to the sheets [16]. The reductive free radicals in the medium react with the reactive functional groups present on the neighboring materials surface. These radicals attack the oxygen rich functional groups on the surface of GO sheets and reduction mechanisms likely lead to re-graphitization within the sites of the previous functional groups and elimination of water molecules. Although it is not intrinsically possible to quantitatively detect the selective mechanisms leading to re-graphitization, it is recently suggested that sp² carbon formation is attributed to the reduction of both epoxy and carbonyl groups because of their better electronic transfers upon reduction [17, 18]. This would mean that hydroxyl groups, almost present on edges of GO sheets and grains most likely tend to form vacancies and micro-pores across the graphitic plans, rather than allowing for re-graphitization.

In view of the above irradiation condition, A potential reaction mechanism leading to the reduction of GO under γ-irradiation is proposed in scheme (2) [19, 20]. The H radicals attack the oxygen atoms of surface epoxy groups and the ring-opening reactions take place converting them to hydroxyl groups. Another H radical reacts with the formed hydroxyl groups leading to the elimination of water and recovering =C conjugated structure (equation 5). The attack of H radicals on the carbonyl groups also leads to the formation of hydroxyl groups, which are removed from the carbon plane via production of water molecules (equation 6). Another possible reaction may occur between two adjacent hydroxyl groups in the interior of aromatic area with two hydrogen
radicals leading to elimination of water and restoring the sp\textsuperscript{2} structure of the carbon plane (equation 7) [21]. Combined with the above FTIR result, the carboxyl and hydroxyl groups are proved to be reduced and removed by γ-ray irradiation. Other pathways may occur during the irradiation process. The reaction of radicals, upon epoxy or carbonyl groups, may lead to either the elimination of the groups and the formation of water or carbon dioxide gas [22]. Radicals may attack aromatic rings leading to their opening or split epoxy bridges and form hydroxyl and C-H bonds [23]. Vacancies generated across the crystalline domains after elimination of carboxylic or hydroxyl groups may lead to recombination of active C radicals into conjugated C-C bonds restoring the sp\textsuperscript{2} structure of the carbon plane. The irradiation of GO is therefore able to induce specific deoxygenation of the surface through the elimination of the most reactive functional groups present on the surface of GO which leads to the reformation of aromatic sp\textsuperscript{2} carbons in the sites of the reduction [21].

Scheme (2) Mechanism of graphene production by radiation

In order to follow the successful steps of the GIG synthesis, UV-Vis spectra and X-ray diffraction measurements have been used during different preparation stages. The UV–Vis spectra of graphene oxide and graphene are shown in Fig. 1. Both materials were dispersed in double distilled water until homogeneously distributed materials were obtained. It is observed that the spectra show a shoulder around 299 nm that corresponds to n→π* transition of C=O bonds for
GO. This shoulder practically disappeared and the absorption peak around 239 nm corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C–C bonds is red-shifted to 276 nm after irradiation for GIG [24]. This is the first indication of the conversion of GO to GIG.

**FIG 1. UV-Vis spectra of GO and RG**

In order to optimize the preparation conditions of GIG and confirm its purity GIG FTIR, Raman and UV-Vis. spectroscopy for structural measurements and FE-SEM and TEM for surface studies were used. In the Raman spectrum of GIG (Fig. 2), the G band was shifted upward to 1594 cm$^{-1}$. At the same time, the intensity of the D band at 1346 cm$^{-1}$ increased markedly due to the significant decrease of the size of the inplane sp$^2$ domains and the partially ordered graphite crystal structure of graphene nanosheets [25]. The appearance of D band peak requires a defect for its activation, so the D band intensity can be used as a measure for the degree of disorder. After their radiation, the $I_D/I_G$ ratio increased substantially from 0.96 to 1.22 during the reduction of GO into GIG suggesting that the $\gamma$-ray irradiation alters the GO structure. Hence, the formation of defects occurs beside the removal of oxide irradiation creates many new graphitic domains in the structure, which are smaller in size, but more numerous in number. Although the amount of reactive groups on the GO surface was reduced, the size of the defective regions didn’t change reasonably after the reduction process. The previously present oxygen rich groups were therefore only partially re-
graphitized and new vacancies were formed both on the edges and across the GIG sheets [26, 27]. It is suggested recently that the reduction of epoxy and carbonyl groups may most likely lead to the formation of sp2 carbon domains while, hydroxyl groups mainly lead to vacancies rather than tending for regraphitization [28, 29]. The formation of multilayered GIG reduces the relative intensity of 2D peak. As the number of layers increases, the full width at half maximum (FWHM) of this peak increases and it is blue shifted [30].

![Raman spectra of GO and GIG](image)

**FIG 2.** Raman spectra of GO and GIG

3.2. Anticorrosion behavior of GIG coated onto AISI 316 stainless steel bares

GIG as anti-corrosive coating for AISI 316 stainless steel in 3.5% NaCl solution and 0.5 M sulfuric acid solution was investigated. To enhance the corrosion protection efficiency of GIG in 3.5% NaCl solution, chitosan (CS) was added to GIG matrix to form GIG/CS composite. PDTI-inhibitor (1-aryl-3-phenylcarbamoyl-8,9-dimethoxy-10b-methyl [1,2,4] triazolo [3,4-a] 1,5,6,10b-tetrahydro-isoquinoline 4 methoxy (Inh) was also used to improve anti corrosion behavior of GIG coatings for protection of AISI 316 in 0.5 M sulfuric acid solution.
3.2.1 EFFECT OF TEMPERATURE ON THE EFFICIENCY OF RG COATINGS

The activation energy of the corrosion reaction in 3.5% NaCl solution is calculated from Arrhenius plots using the following equation:

\[ i_{corr} = A e^{E_a / RT} \]

Where \( E_a \) is the activation energy, \( T \) is the absolute temperature, \( A \) is the frequency factor, \( R \) is the gas constant and \( i_{corr} \) is the corrosion current density.

Fig. 3 represents the relations between \( \log i_{corr} \) versus \( 1/T \) for different surfaces. The values of \( E_a \) was calculated from the slopes of the straight lines relationships obtained in Fig 3. The calculated value of the corrosion activation energy of bare SS 316, GIG and GIG/CS are 2.92, 5.23 and 6.76 kJ mol\(^{-1}\), respectively. These values agree with the order of protection efficiencies confirming the protective efficiency of GIG and GIG/CS. It is concluded that GIG/CS has enhanced the corrosion protection compared to GIG as the temperature increases.

**FIG 3.** Variation of \( \log i_{corr} \) with \( 1/T \) for bare SS 316, GIG and GIG/CS in 3.5%NaCl at different temperature.
The activation energy of the corrosion reaction in 0.5 M H₂SO₄ solution was also calculated from Arrhenius plots.

The values of the activation energies obtained are 2.15 kJ mol⁻¹, 3.34 kJ mol⁻¹ and 7.29 kJ mol⁻¹ for the bare, GIG-coated and GIG/2 mM Inh, respectively. From the data, it is concluded that the highest protection efficiency is exhibited when using GIG/2 mM Inh; 93.5% - 95.8% protection efficiencies for the temperature range studied was recorded.

The thermodynamic parameters were calculated using the transition state equation [31]:

\[
\log \left( \frac{j_{corr}}{T} \right) = \log \left( \frac{R}{Nh} \right) + \frac{\Delta S^o_a}{2.303 R} - \frac{\Delta H^o_a}{2.303 RT}
\]
where $N$ is the Avogadro’s number, $h$ is the Planck’s constant, $\Delta S^\circ_a$ is the entropy of activation and $\Delta H^\circ_a$ is the standard enthalpy of activation. Hence, a plot of $\log (j_{\text{corr}}/T)$ against $1/T$ yields a straight line.

The standard enthalpy change can be evaluated from the slope to be 2.36, 5.10 and 14.2 kJ mol$^{-1}$ for bare AISI 316, GIG and GIG/2 mM Inh, respectively. The standard entropy of activation was calculated from the intercept to be -331, -333 and -317 J mol$^{-1}$ K$^{-1}$ for bare AISI 316, GIG and GIG/2 mM Inh, respectively.

3.2.2 SURFACE MORPHOLOGY OF COATED METALS AFTER 3.5% NaCl SOLUTION IMMERSION

The FE-SEM was used to examine the morphology of the stainless steel surface with coatings before and after exposure to the chloride solution under polarization conditions. Fig. 4(A), and (B) show the surface morphology of bare SS, coated with GIG and SS coated with GIG/CS, respectively after immersion for 2 hours in 3.5% NaCl solution and subjected to potentiodynamic polarization test. Fig. 4(C) and (D) show the steel surface after removing the GIG and GIG/CS coatings, respectively. It is observed that the GIG and GIG/CS offer effective coatings for the surface and no pitting spots were observed on the surface. It is important to mention that some “black” spots appear in the images of the SEM that mainly correspond to the left parts of graphene after peeling the layer off the surface of steel.

3.2.3. EFFECT OF PROLONGED IMMERSION TIME IN 0.5 M SULFURIC ACID ON COATED AND NON-COATED SS BARES

The effect of immersion time of the bare AISI 316 surface in 0.5 M sulfuric acid was studied to elucidate the stability of the oxide film and the obtained Nyquist and Bode plots as given in Fig. 5. The corresponding semicircles of the Nyquist plots of Fig. 5
show noticeable decrease in radius as the time of immersion increases. As the time of immersion is extended (up to three days), both $R_{ct}$ and $R_{f}$ values decrease appreciably indicating the breakdown and dissolution of the passive barrier oxide layer off the surface of the stainless steel. The film resistance decreased from $1.4 \times 10^3 \, \Omega \, \text{cm}^2$ at immersion 0 hour to $107 \, \Omega \, \text{cm}^2$ after immersion for 72 hours while the charge transfer resistance decreased from $560 \, \Omega \, \text{cm}^2$ to $500 \, \Omega \, \text{cm}^2$ after immersion for 72 hours.
FIG 5. Nyquist plots of bare AISI 316 after prolonged immersion times in 0.5 M H$_2$SO$_4$ solution at 298 K.

On the other hand, the Nyquist and Bode plots for AISI 316 coated with GIG and GIG/2mM Inh after immersion for different times in 0.5 M sulfuric acid are represented in Fig. 6 and 7 respectively. The GIG and GIG/2 mM Inh-coated surfaces showed a decrease of the values of the charge transfer resistance. The charge transfer resistance for GIG coated stainless steel decreased from 2.3x10$^3$ Ω cm$^2$ to 2.0x10$^3$ Ω cm$^2$ when the immersion time increased from 0 to 72 hours. While it decreased from 1.21x10$^4$ Ω cm$^2$ to 7.08x10$^3$ Ω cm$^2$ in case of steel coated with GIG/2 mM Inh after extending the immersion time to 72 hours. Also, it was found that the values of the charge transfer resistance were relatively higher for the GIG containing inhibitor while maintaining protection efficiencies exceeding 90%. This confirms the protection efficiencies of the GIG coupled with the use of the inhibitor to prevent corrosion of AISI 316 in acidic medium.
FIG. 6. Nyquist plots of GIG after prolonged immersion times in 0.5 M H₂SO₄ solution at 298 K

FIG. 7. Nyquist plots of GIG/2 mM Inh after prolonged immersion times in 0.5 M H₂SO₄ solution at 298 K
4. CONCLUSION

Gamma radiation was used for reduction GO to graphene without any further use of chemicals as reducing agents. The surface and structural studies proved the high purity and quality of the prepared GIG using this technique. The prepared GIG was used as an effective anticorrosive coating for protection of AISI 316 stainless steel in aggressive chloride containing solutions and acidic medium. GIG was further modified through the inclusion of chitosan CS into GIG matrix to form GIG/CS composite. The electrochemical studies including potentiodynamic polarization and EIS measurements proved high protection efficiency offered by these coatings in 3.5% NaCl solution. The corrosion current in case of GIG and GIG/CS coatings was one order of magnitude higher than the corresponding value of bare AISI 316. When studying the effect of temperature, the apparent activation energy of bare AISI 316, GIG and GIG/CS were 2.92, 5.23 and 6.76 kJ mol\(^{-1}\), respectively. All these findings confirm the high protection efficiency of the coatings. On the other hand, surface studies revealed the exposure of bare steel surface to pitting corrosion after immersion in 3.5% NaCl solution, while the examination of coated surfaces after removal of GIG and GIG/CS coatings showed intact steel surface which was free of pitting spots. EIS measurements indicated higher resistance for GIG and GIG/CS coatings than the bare steel and confirmed the stability of the coatings after different immersion times in NaCl solution. The values of Ret were higher for GIG and GIG/CS coated stainless steel compared to the bare surface and GIG/CS showed relatively higher values compared to GIG confirming the synergistic effect of CS with respect to the protection efficiency. Corrosion behavior of GIG coating on AISI 316 was investigated in 0.5M sulfuric acid solution. Different concentrations of PDTI-inhibitor were loaded on GIG sheets to enhance the protection efficiency of GIG. The successful incorporation of inhibitor molecules was confirmed using FTIR spectroscopy and TEM. Potentiodynamic polarization and EIS measurements indicated that the protection efficiency was enhanced upon using the PDT Inhibitor with GIG and the efficiency increased (up to 95%) with increasing the inhibitor concentration.
REFERENCES


FRANCE

"RADIATION-INDUCED ELABORATION OF NANOCOMPOSITES IN DIMENSIONALLY CONTROLLED MACRO- OR MICRO- STRUCTURES"

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1. Introduction

Additive manufacturing methods, particularly 3D printing are predicted to grow rapidly and substantially, in many sectors of industry. The current development of cheaper and highly performant production equipment as well as the large offer in starting materials result in a considerable increase of number of end-user industries exploiting these technologies [1].

3D printing includes various types of iterative and computer assisted elaboration of three-dimensional objects by joining powder grains or solidifying reactive or meltable materials typically layer by layer. The precision, repeatability and processable starting material are still key challenges. In addition, the technology suffers from some limitations in terms of intrinsic mechanical performance and from the need of additional functionality for the 3D materials. Various domains of application, such as biomedical devices, microfluidics, electro-optics, measuring instrumentation and sensorics, are expecting new technological developments to meet their current needs.

Based on the previous experience of our Institute in radiation processing of nanoparticles, nanocomposites and nanostructured materials, we will contribute to the CRP by combining radiation-induced chemistry and 3D printing with various techniques, to improve the mechanical performances and/or to impart additional functionalities through a rational use of radiation processing, structuring or modifying materials at nanoscale.
2. Background activities and achievements

2.1. Nanoparticles and nanocomposites based on cellulose

*Nanocrystalline cellulose*. The growing interest for green and sustainable chemistry covers the various constituents of biomass as a promising, renewable and vast source of chemicals and materials. In particular, cellulose nanocrystals (CNC) obtained by controlled acid hydrolysis of natural fibers exhibit outstanding structural and mechanical properties [2]. CNCs were obtained from pre-treated ramie (Boehmeria nivea) fibers by appropriate hydrolytic fractionation in concentrated sulfuric acid and subsequent purification by dialysis [3]. The final aqueous suspensions of CNCs have a typical dry matter content of 3-4 wt-%. The applicability and the relevance of radiation processing for obtaining materials with improved or with new properties was evaluated by performing one study on radiation cured nanocomposites including CNCs and on the radiation-induced graft polymerization at the surface of CNCs.

*Radiation-cured polyurethane acrylate composites including cellulose nanocrystals* [4]. The unique features of nanocrystalline cellulose have been recently exploited for obtaining nanocomposites by blending CNC with various thermoplastic or thermoset materials [5]. Very few articles report on the use of CNCs as nanofillers in radiation-curable formulations [6]. As the matrix precursor a commercial water – based polyurethane (PUR) acrylate (PURa) emulsion was selected for our studies (Fig. 1). This approach allows for the use of water as a common phase for mixing and casting the curable formulations in molds. Films of thickness ranging from 1 to 2 mm could be easily obtained by this method. Two types of radiation commonly used for the processing of paints, coatings, inks and adhesives were applied, (i) high intensity UV-vis LED emitting at 395 nm and (ii) low energy Electron Beam (EB). A photoinitiator was introduced to the formulations prepared for UV-vis curing. FTIR in the medium (MIR) and near visible range (NIR) was used for determining the conversion of monomer. The influence of the amount of cellulose nanoparticles (1 to 10 wt%) was studied by various physical and mechanical measurement including DMA and tensile tests.
The nanocomposites with 1 – 10 wt-% of CNCs were obtained as transparent materials after drying under mild conditions (Fig. 2). Cross-linking polymerization of samples prepared in the form of films or of 1 mm-thick bars was either initiated by exposure to the 395 nm light of a high intensity LED lamp or by treatment with low energy electron beam (EB). The conversion level of acrylate functions in samples submitted to increasing radiation doses was monitored by Fourier Transform Infrared Spectroscopy (for thin samples, NIR for thick films of bars). The profile of the reaction kinetics measured during UV-initiated polymerization was not significantly altered by the presence of the nanocrystals in the coalesced material.

Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) were used to characterize changes in the glass transition temperature of the PUR-CNC nanocomposites as a function of acrylate conversion and of CNC content. Mechanical tests show that significant improvements of tensile Young’s modulus and tensile strength at break σ were achieved by introducing cellulose nanocrystals in amount as low as 1 wt-% in the PUR acrylate material.

Micromechanical testing indicates the positive effect of 1 wt-% CNC on Young’s modulus and on the tensile strength at break) of cured nanocomposites. The presence of CNC in the PUR acrylate matrix was shown to double the σ value of the nanocomposite cured to an acrylate conversion level of 85 % by treatment with a 25 kGy dose under EB irradiation, whereas no increase of σ was observed in UV-cured samples exhibiting the same acrylate conversion level. The occurrence of grafting reactions inducing covalent linkages between the polysaccharide nanofiller and the PUR acrylate matrix during the EB treatment is advanced as the most probable explanation to account for the improvement observed in samples cured under ionizing radiation.

*Stimuli-responsive cellulose nanocrystals by radiation-induced graft polymerization of N-isopropyl acrylamide.* Surface modification is a key strategy for tailoring the properties and the behavior of nanoparticles in specific environments. Cellulose nanocrystals (CNC) exhibit at their surface a large density of potentially reactive anhydroglucose units, while having a very stable core structure and unique aspect ratio [7]. Various methods have been used to convert the hydrophilic and polar surface of the CNC by ionic interactions with surfactants, by chemical coupling to hydroxyl groups or by polymer grafting. However, radiation grafting onto NCC seems to have received little attention in the literature, despite its unique advantages [8, 9].
The graft polymerization of N-isopropyl acrylamide (NIPAM) onto cellulosic materials was studied for obtaining thermo-responsive grafts at the surface of the nanowhiskers. Such a surface modification is expected to induce new properties such as colloidal stability at high ionic strength, surface activity, and thermally triggered dispersion and aggregation in aqueous media [10].

CNC suspensions were irradiated in the presence of air at various irradiation doses using electron beam accelerator. Radiation processing of CNCs generates C-centered free radicals, that are converted into peroxides and hydroperoxides for achieving free radical graft polymerization in a subsequent stage.

Free-radical initiation was activated on-demand by the Fenton reaction applied to peroxidized CNC in the aqueous monomer solution. The amount of grafted polyNIPAM was determined by elemental analysis on the basis of the nitrogen content (1 - 10 wt-%) which can be adjusted by varying the grafting conditions. The dry state dimensions of raw and grafted CNCs were estimated after careful purification using atomic force microscopy in different modes including nanoIR analysis which confirmed the presence of polyNIPAM attached to CNCs. DLS allowed to study the variations of the apparent hydrodynamic radius for grafted CNCs as a function of temperature, at various pH and for different polyNIPAM contents. Turbidity measurements also indicated the reversible aggregation of grafted CNCs in aqueous suspensions upon heating above the transition temperature (32 - 35°C).


Since the early stages of research in nanoscience, the radiation-matter interaction has been exploited to develop nanoparticles from aqueous solutions of metallic cations [12]. The solvated electrons (e\textsuperscript{-aq}) generated by the interaction with radiation in high energy reduce metallic ions by a complex sequence of reactions [13].

To prevent the aggregation of nanoparticles, the addition of a colloidal stabilizer is necessary. Chitosan was chosen because of its good adsorption onto the nanoparticles and because of the resultant interparticle repulsion due to its cationic polyelectrolyte properties [14]. The objective of
this work is to investigate the specific role of chitosan in the radiation (EB, gamma) synthesis of gold nanoparticles with well-defined characteristics.

Gold nanoparticles were prepared by irradiation of a HAuCl\textsubscript{4} solution in the presence of chitosan. The solutions were characterized after irradiation by UV-vis and by quasi elastic light scattering (DLS). Initial results show the appearance of an absorption band around 525 nm characteristic of the formation of gold nanoparticles [15,16]. We investigated the influence of dose, samples conditioning (under air or argon) and the role of free radical scavengers on the rate of reduction process, on the dimensional characteristics of particles and on the aging of colloidal suspensions. Deeper understanding of the mechanisms involved in the elaboration of nanoparticles required additional information on the processes taking place before and during the reduction of ion AuCl\textsubscript{4}. In order to apprehend the effects directly related to the irradiated chitosan and its involvement in the reduction process. The results presented and discussed in this paper allow for concluding to:

- the effective complexation of Au (III) by chitosan in the solution prior to irradiation [17],
- strong dose rate effects on nanoparticle formation [18],
- the significant contribution of chitosan-mediated reduction of Au (III) to the overall process of nanoparticle formation, as exemplified by the efficient quenching of nitrous oxide (N\textsubscript{2}O) upon irradiation of Au (III) solutions, whereas in the presence of chitosan, Au nanoparticles were formed in significant amount in aqueous solution saturated with N\textsubscript{2}O treated with a 5 kGy EB dose [11].


Lignin is a class of natural polymer exhibiting unique structural features in many respects. Essentially considered as a low-value by-product of the pulping industry, lignins currently receive increasing attention for their potential use as new feedstock for obtaining biobased solvents, surfactants, anti-oxidants and prepolymers.

The potentialities of various types of raw and fractionated lignins as photoresist materials for one-photon (at 395 nm) and two-photon (at 780 nm) lithography were assessed by comparing their merits in terms of practical sensitivity and on molecular reactivity. Lignin can be dissolved in
substantial amounts into appropriate solvents for preparing thin negative-tone photoresist films with good uniformity allowing for precise analysis of their photochemical behavior upon one- or two-photon excitation in the solid state.

The influence of lignin structure and molecular weight on their photoreactivity was examined by using various spectroscopic and analytic methods. Mechanistic pathways for the curing process can be proposed to account for the correlated decrease of the methoxy groups of the guaiacyl units and the formation of carbonyl groups.

The sensitivity, resolution, and contrast of a series of lignin samples were determined by photocuring experiments conducted in air and in nitrogen under the frontal beam of a UV-visible LED (395 nm).

Lignin samples selected for their promising performances assessed by one-photon curing experiments were also shown to produce well-resolved 3D-nanostructures using a two-photon direct laser writing equipment.

2.4. Nanoheterogeneities in radiation-cured matrices for high performance composites

Besides the research activities on bio-based polymers and materials, research projects are on-going on the radiation-initiated crosslinking polymerization for high performance composites and for lithography.

The polymerization of multi-acrylate monomer compositions under exposure to UV-visible light or is known to proceed heterogeneously at various dimension scales, depending of monomer composition. In radiation-cured materials based on a single type of monomer, the network was shown to display heterogeneities of cross-link densities resulting from a complex interplay between mechanistic and kinetic factors along the solidification process [20, 21].

Compared to free-radical chain polymerization, radiation-initiated cationic polymerization exhibits peculiarities at the different steps of the chain process (complex initiation and propagation mechanisms, pseudo-living character, …). The influence of these features on the reactivity and on the microstructure of multifunctional aromatic epoxy monomers and of their acrylate analogues has been examined using various types of radiation (UV, visible, EB, X-ray). Complementary
spectroscopic and analytical methods were implemented to correlate the changes of network physical properties as a function of the polymerization degree.

AFM analysis of the networks in the topographic, phase contrast and indentation modes provides quite informative data with indications on the actual dimensions of the soft and rigid domains and of their evolution, as the curing level is driven to higher values.

Based on these observations and measurements, a consistent scenario for the build-up of radiation-cured networks is proposed [22, 23].

To improve composite damage tolerance, original acrylate-based formulations with improved mechanical resistance were developed by using thermoplastic additives. Phase separation takes place during radiation-initiated polymerization, yielding toughened resins with KIC values over 2 MPa.m0.5 while it was measured at about 1 MPa.m0.5 for the unmodified epoxyacrylate resin. By studying the related toughening mechanisms, this improvement was found to be linked with the nanoscale features of the matrix morphology. High Tg values (over 160°C) are also reachable in conjunction with high toughness. Flexural properties are also satisfactory with corresponding moduli above 3 GPa. In addition, the low viscosity of some of these systems makes them very interesting for liquid based processes, such as Resin Transfer Molding (RTM) since the viscosity falls down to less than 1 Pa.s above 60°C, with still significant injection window. To demonstrate the feasibility of all the process sequence and to evaluate composite properties, a carbon-fiber reinforced plate showing superior damage tolerance was successfully manufactured using the RTM technique and X-ray initiated polymerization [24, 25].

The radiation-initiated cationic polymerization of epoxies and vinyl ethers continues to receive considerable interest since the original discovery of the potentialities of onium salts as initiators. Onium salts with a low nucleophilicity counter anion can be activated by thermal, photochemical and radiochemical activation. Efficient Bronsted or Lewis acids are generated via different mechanisms and efficiently initiate the chain polymerization of epoxy functions or of other cationically polymerizable monomers.

The assets of this chemistry continue to stimulate research on initiators systems and on application-oriented projects, but the current knowledge on the relations between reactivity, microstructure and properties is limited. In the frame of our current research on epoxy homopolymerization and its potentialities in the field of high-performance composite materials and in nanolithography, we
are currently investigating the thermal and microstructural aspects of the cationic polymerization of model aromatic epoxies, using AFM for investigating the network heterogeneities in terms of variations of local moduli and adhesion properties [26].

3. Project description and implementation

The proposed research activity aims at studying the potentiality of radiation processing for the synthesis of nanocomposites forming or included in 1D to 3D structures (i.e. 1D: line, fibre or bar, 2D: grid, mesh, mosaic substrates, 3D: scaffold, prepared by molding, by lithography or by 3D printing).

Various types of chemical reactions will be considered and implemented, depending on the orientations of collaborative actions within the CRP:

- grafting reactions (from /onto) inorganic or organic nanoparticles,
- cross-linking polymerization of monomer blends including metal or inorganic nanoparticles,
- radiation-induced formation of nanoparticles by in-situ reduction (e.g. metal ions or graphene oxide) on the properties of organic nanocomposites including cellulose nanowhiskers or carbon nanotubes particles.

The diverse synthetic reactions listed above constitute an effective toolbox for elaborating nanocomposites constituting or included in structured materials (1 to 3 D, as defined above).

The functionalities associated with the nanocomposites may relate to some specific features such as optical properties, electrical or thermal conductivity, stimuli responsiveness, fire-resistance, biocompatibility, etc.

3.1 Research objectives

The contribution of our Institute to the CRP project primarily aims at studying the potentiality of radiation processing for the synthesis of nanocomposites forming, or included in, 1D to 3D structures (i.e. 1D: line, fibre or bar, 2D: grid, mesh, mosaic substrates, 3D: scaffold, prepared by molding, by lithography or by 3D printing).
Various types of chemical reactions will be considered and implemented, depending on the orientations of collaborative actions within the CRP:

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The functionalities associated with the nanocomposites may relate to some specific features such as optical properties, electrical or thermal conductivity, stimuli responsiveness, fire-resistance, biocompatibility, etc.

3.2 Scientific scope

The work plan encompasses the study of various basic aspects of radiation-induced reactions (kinetics and mechanistic aspects), establishing structure-properties relationships, evaluating and optimizing functionalities of technological interest. During the last two years,

The scientific aspects of the studies include more specifically:

- selection and control of key parameters relating to radiation processing
- kinetic and mechanistic study of the key reactions
- investigation on the combined effects of chemical composition and processing on the structure of the nanocomposites forming or included in the 1 to 3D structures
- establishment of structure-properties relationships for the nanocomposites and for the global systems
3.3 Workplan

The proposed working plan articulates research activities in 3 stages, with an exploratory investigation of the most promising paths expressed during the 1st RCM, including the monitoring of key reactions and phenomena controlling main features of the nanomaterials (i.e. composition, size, …) for Year 1, advanced reaction monitoring, mechanistic investigations and application to simple 1D and 2D demonstrators of the second year, with gradual transfer of the main findings to the design of materials and systems with dedicated technological functionality.

- Year 1
  - Exploratory investigation and feasibility demonstration for the various approaches based on radiation-induced elaboration of nanoparticles, modified nanoparticles and nanocomposites
  - Monitoring of reactions - Fine characterization of the nanomaterials and nanocomposites
  - Determination of key factors and of challenges in terms of functionality and performance
    (to be precisely defined depending on the main orientations of the CRP program)

- Year 2
  - Continuation of the work on reaction monitoring and on the characterization of obtained materials
  - In-depth study of key parameters defined during the exploratory approach
  - Adaptation of the synthetic methods to the fabrication of 1 to 3D demonstrators
  - Definition of technological targets - work plan for reaching the technological objectives

- Years 3 and 4
• Finalization of basic studies for preparing scientific articles reporting on the achievements of the research
• Optimization of the properties of technological interest
• Increase in scientific knowledge, particularly on mechanistic and kinetics aspects of the radiation-induced reactions:
  - Advances in the structural characterization of the nanocomposites
  - Innovative design and fabrication of 2D and 3D structures including nanocomposites for targeted applications
• IP protection and transfer

3.4 Facilities and equipment available for the project
Besides conventional chemistry labs, the following equipments and facilities will be used for accomplishing the tasks detailed above:

• Radiation equipment
  Low energy (80-150 kV) self-shielded accelerator
  Various UV and UV-visible sources
  Access to 10 MeV Linac at Ionisos facility in Chaumesnil, France
  Access to a Nanoscribe 780 nm laser writing equipment au UTT in Troyes, France

• 3D-printing
  Platform PLATINIUM3D and lab equipments at ISI
  Fused deposition modeling FDM, Selective Laser Sintering SLS, Stereolithography SLA

• Analytics and spectroscopy
SEC and HPLC
DSC, DMA, UV-visible, MIR and NIR spectroscopies, mechanical testing
NMR platform (solid, liquid, cryoplatform), MS platform, X-ray diffractometers, DLS

- Access to nanoscale characterization equipment in URCA’s platforms
  SEM, TEM, AFM at NanoMat’ platform and the Laboratory for research in nanoscience

4. Conclusion
The CRP aiming at 'Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology' provides a unique opportunity to share with the other partners the ambition to develop new aspects of additive manufacturing by introducing relevant radiation processing steps in the fabrication of advance and dimensionally structured materials.

Basic aspects of radiation chemistry will be exploited and developed in that perspective. The richness of the partnership gathered by IAEA within this CRP should allow very useful collaborations by bringing together various expert team on focused research activities with well identified scientific and technological objectives.

REFERENCES


INDONESIA

SYNTHESIS OF NANO CHITOSAN-MICROBIAL CELLULOSE (CH-MC) COMPOSITE FOR SPLINT TEETH IN PERIODONTAL

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Abstract
Tooth and mouth disease are one of serious health problem in Indonesia. It was reported that the prevalence of tooth and mouth disease in Indonesia in 2013 is 25.9% including chronic periodontal and tooth mobility, and the incident increases every year. Periodontal disease is considered as an infectious pathology caused by the interaction between a susceptible host and bacterial factors present in dental plaque. One of the techniques to immobilize and stabilize the injured teeth is by splint periodontal. Depending on the duration of use, splints are classified as temporary, provisional or permanent and may be either fixed or removable. Splint can be a rigid or flexible device that maintains in position a displaced or movable part. Rigid splint has disadvantages such as stress shielding effect takes place in the plated area. The use of flexible splint increasing attention of researchers. Non-rigid fixation allowing physiologic tooth mobility has been shown to be desirable for periodontal healing. A flexible splint of short duration appears to reduce the risk of dentoalveolar ankylosis or external replacement resorption. Currently there are a number of fiber reinforcement materials available on the market. Among them are glass fibers and polyethylene fibers. In Indonesia, these materials have expensive price which is USD 50 to 150 per piece which make inaccessible for the poor people and most of these products are imported product. The initiative to prepare splint material from natural polymers such as chitosan and cellulose microbial is proposed in this project.

Keywords: splint periodontal, chitosan, microbial cellulose, gamma radiation, tooth mobility

1. OBJECTIVE OF THE RESEARCH
The aim of the proposed project is to study characteristics of the splinting periodontal from nano-chitosan-microbial cellulose sterilized by radiation for application in periodontal
2. INTRODUCTION

Health Research and Development Agency, Ministry of Health Republic of Indonesia reported that the prevalence of tooth and mouth disease in Indonesia in 2013 is 25.9%. Chronic periodontitis and tooth mobility are about 8% of the totals tooth and mouth diseases, and the incident increases every year [1]. Periodontal disease is considered as an infectious pathology caused by the interaction between a susceptible host and bacterial factors present in dental plaque [2]. Periodontal disease can cause reduction of periodontal attachment which result in tooth mobility and migration, causing misaligned occlusal forces that hinder the balance between bone resorption and bone remodeling and the reorganization of periodontal fibres. Tooth mobility can be defined as visually perceptible movement of the tooth away from its normal position when a light force is applied or movement of a tooth in a horizontal or vertical plane of space. Tooth mobility usually is the result of occlusal trauma associated with periodontal disease. The continued movement of the mobile tooth during oral function further damages the periodontium, accelerating the disease process thereby leading to tooth loss [3]. Furthermore, increased tooth mobility adversely affects function, aesthetics, and the patient’s comfort. It was accepted that tooth mobility contributed to attachment loss and the formation of vertical osseous defects. Increased mobility of teeth was a direct consequence of traumatic occlusion, bruxism, and clenching [4]. One of the techniques to immobilize and stabilize the injured teeth is by splint periodontal [4]. Splint can be a rigid or flexible device that maintains in position a displaced or movable part. Fiber reinforcement materials such as glass fibers and polyethylene fibers are being used in splinting technique. It has been proven that while a splint is in place, there is a reduction in tooth mobility. Once the splint is removed, the mobility is unchanged [4]. Depending on the duration of use, splints are classified as temporary, provisional or permanent and may be either fixed or removable. Occlusal splints can be classified as provisional or definitive depending on the type of materials used and the intended duration the splint will be in place for [5]. An ideal splint materials should have the following criteria such as: should be stable and efficient, easily repaired; should permit good plaque control; should not hamper periodontal instrumentation; should be non-irritating to the tissues; should be esthetically acceptable; for every mobile tooth, at least two firm teeth should be present [5, 6].
The simplest way to connect teeth to each other is the classic bonding method. The enamel surface of the tooth is etched, most commonly with 37% phosphoric acid. Composite resin can then be bonded to the etched surface and used to rigidly connect the teeth to each other. The composite resin splint can be strengthened by adding fibers to the splint or by using a fiber meshwork, e.g., Ribbond to reinforce the material. These splinting methods that attract more plaque, complicate oral hygiene and further compromise esthetics are obsolete and are to be avoided [5], more over, this method also result in the fractured composite between the teeth [4]. To overcome these problems, some attempts have been made by introduction fiber reinforcement materials such as glass fibers and polyethylene fibers which has a high strength, bondable, biocompatible, esthetic, easily manipulated, colorless ribbon fiber reinforcement material that could be embedded into a resin structure. Currently there are a number of fiber reinforcement materials available on the market. Among them are glass fibers and polyethylene fibers. In Indonesia, these materials have expensive price which is USD 50 to 150 per piece which make inaccessible for the poor people and most of these products are imported product. The initiative to prepare splint material from natural polymers such as chitosan and cellulose microbial is proposed in this project. It is hope that by using these materials and radiation technology to induce low molecular weight (LMW) chitosan and sterilized the product as well, it can reduce the price and can be a product substitution import.

Microbial cellulose (MC) or bacterial cellulose is an exopolysaccharide produced by various species of bacteria, such as Acetobacter, Agrobacterium, and Aerobacter [7]. MC is preferred over the plant cellulose as it can be obtained in higher purity and exhibits a higher degree of polymerization and crystallinity index [8]. It also has higher tensile strength and water holding capacity than that of plant cellulose. The typical Young’s modulus of MC is found to be in the range 15–35 GPa, with the tensile strength in the range 200–300 MPa [8-10]. MC exists as a basic structure known as microfibrils, which are composed of glucan chains interlocked by hydrogen bonds so that a crystalline domain is produced. Fibrils of bacterial cellulose are about 100 times thinner than that of plant cellulose, making it a highly porous material and surface area, which allows transfer of antibiotics, chitosan or other substances [10]. In our previous works, microbial cellulose was prepared using A. xylinum under growth medium consisting of coconut water, ammonium sulphate, and sucrose incubated at 30°C. The MC has high mechanical properties, nano fiber structure and high thermal decomposition [11,12]. Besides
having excellent properties, MC has the disadvantage such as does not have anti-bacterial and anti-inflammatory properties.

Chitosan [poly(1,4)-/3-D-glucopyranosamine], a natural polysaccharide, which is widely present among marine and terrestrial invertebrates. Chitosan could normally be obtained from crab or shrimp shells, by alkaline deacetylation of chitin [13]. This biopolymer has a number of chemical and biological properties such as consisting of linear polyamine, it has reactive amino groups (-NH2) and hydroxyl groups (-OH), it has chelating ability for many transitional metal ions, biocompatible, non toxic, Accelerates the formation of osteoblast, responsible for bone formation, haemostatic (causes stop bleeding), fungistatic (inhibiting the growth of fungi), spermicidal (birth control), bacteriostatic, anti-inflammatory and anti cancer, [14]. It makes chitosan potential to be use as biomaterial. It was reported that low molecular weight (LMW) chitosan showing higher activity to bacteria and mold compared to high molecular weight. High energy irradiation such as gamma rays and electron beam is an effective tool for preparing LMW chitosan. Chitosan nanoparticles can be prepared by ionic gelation method using Tripolyphosphate (TPP) as crosslinking agent [15-17]. From these properties of MC, nano chitosan could be incorporated into the MC structure and induced a composite which can be used as splint material in periodontal application.

3. MATERIALS AND METHODS

3.1. Materials

Chitosan produce by BATAN with DD of 85-90% and Mw of 250-300 kDa, tripoly-phosphate (TPP), ammonium sulphate, sodium hydroxide, hydrochloride acid, coconut water, sugar cane (sucrose), sodium hypochloride, A.xylinum, TWEEN 80, KBr, glycerol, acetic acid, and others chemical needed.

3.2. Methods

Chitosan was prepared from shrimp shell waste through demineralization and deproteinization by chemically treatment using dilute solution of hydrochloride acid and sodium hydroxide to get chitin. The chitin was then deacetylated by sodium hydroxide to produced chitosan. To reduce molecular weight of chitosan, gamma radiation was used with different doses.
Irradiated chitosan was then crosslinked by tripolyphosphate at different chitosan TPP ration and conditions. The resulted chitosan nano particle was then freeze dried and used for characterization and next processes.

3.3. Characterization of nano chitosan-microbial cellulose.

The physico-chemical, mechanical, biological properties, toxicity and sterility, in vivo evaluation of nano chitosan-microbial cellulose will be evaluated under this project.

4. OUTCOMES

This project is expected to improve the accessibility of patients on the splinting periodontal especially produced from nano chitosan-microbial cellulose sterile radiation for the treatment of periodontal disease.

5. WORK PLAN

5.1. PREPARATION OF NANO-CHITOSAN BY IONIC GELATION METHOD USING TRIPOLYPHOSPHATE (TPP) AS CROSSLINKING AGENT.

Chitosan prepared from shrimp shell was irradiated by gamma rays at different doses (25, 50 and 100 kGy) to reduce molecular weight. It was then reacted with Tripolyphosphate (TPP) with certain composition to get nano size particle. Characterization of nano chitosan properties:

1) Degree of Deacetylation (DD) using Fourier-transform infrared spectroscopy (FTIR)
2) Molecular weight of irradiated and non-irradiated chitosan using Viscometer and or Gel permeation chromatography (GPC)
3) Particle size, polydispersity index (PDI), and surface charge (zeta potential), using Particle size analyzer (PSA)
4) Functional group by Fourier-transform infrared spectroscopy (FTIR)
5) Surface area by Brunauer-Emmett-Teller (BET)
5.2. SYNTHESIS OF NANO CHITOSAN (NCS)-MICROBIAL CELLULOSE (MC) COMPOSITE

NCS-MC COMPOSITE WAS SYNTHESIZED BY TWO STEPS:

1) Preparation of MC pellicle

MC pellicle was prepared by incubation of *A. xylinum* into growth media consisting of coconut water, ammonium sulphate and sugar in special tray at ambient temperature (30 ± 2°C) until growth of pellicle of microbially-derived cellulose was completed. The pellicle was removed from the trays and chemically treated to remove bacterial by-products and residual media. The pellicle was then rinse with filtered water and followed by bleaching to get white pellicle was then rinse thoroughly with filtered water for 2 hours. The final pellicle was then freeze dried to remove the water.

2) Immobilization of NCS into MC pellicle

Dried MC pellicles were put into water suspension of NCS for a certain time to absorb the nano particle of CS. The NCS-MC was then freeze dried to remove the water from the composite. The composite was then sterilized using gamma rays.

Characterization of NCS-MC composite
a) Surface morphology by SEM/TEM
b) Swelling properties in SBF by gravimetric method
c) Particle size, Polydispersity index (PDI) and surface charge (zeta potential using PSA/DLS
d) Functional group by FTIR
e) Surface area by Brunauer-Emmett-Teller (BET)
f) Mechanical properties such as TS, Modulus young, shear strength, peel strength measured by using Universal Testing machine (UTM)
g) Sterility test
h) Toxicity and biocompatibility
i) In-vivo evaluation using animal test
j) Clinical evaluation

3) In situ preparation of nano-chitosan (NCS)-microbial cellulose (MC) composite

Instead of immobilization method as described above, NCS-MC will also be prepared by in situ supplementing chitosan in the culture medium

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ITALY

APPLICATION OF NANOTECHNOLOGY AND RADIATION PROCESSING IN THE DEVELOPMENT OF ADVANCED MATERIALS FOR FOOD PACKAGING SECTOR (NANORADFORPACK)

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Abstract
The exploitation of the combined use of nanotechnology and radiation processing to fabricate advanced food packaging materials will certainly contribute to reach the following objectives: i) to prevent/reduce food spoilage and food waste as it moves from producers to consumers; ii) to extend food shelf life; iii) to meet the consumers demands of food quality and safety; iv) to balance innovation with cost-efficiency.

These goals will be reached by studying, developing and characterizing the following innovative and advanced materials: antimicrobial packaging, antioxidant packaging, nanocomposite films and high barrier packaging. The proposed materials will be produced in the frame of the proposed research agreement proposal by using the following strategies:

- by developing new active nanoparticles, mainly based on cellulose nanocrystals, in which the antioxidant activity is imparted through ionizing radiation
- by embedding these developed active nanoparticles into the polymeric materials
- by using radiation technology to control the release kinetics of (nano)antimicrobial compounds from the active polymer films
- by using radiation technology (ebeam) to irradiate foodstuff pre-packed with nanocomposite polymer films.

Introduction and State of Art
It is well known that active packaging materials are able to positively interact with the packaged food, being able to slow down or inhibit those phenomena which are responsible for the food
unacceptability. Among them, antimicrobial and antioxidant packaging films are particularly interesting for both academic researches and industrial applications. Food deterioration usually starts on food surfaces because of the presence and growth of spoilage or pathogenic microorganisms. Thus, there has been great interest in developing antimicrobial packaging materials that adequately release antimicrobial and antioxidant agents to the surface of food, thus inhibiting microbial contamination during storage and oxidation reaction.

As for the antimicrobial agents, they are often directly applied to foods using dipping, dusting, or spraying to prevent surface contamination of food. Direct application of antimicrobial agents on food surfaces has some limitations because the antimicrobial agents can be neutralized, evaporated or diffused inadequately into the bulk of food. The idea to be exploited in the frame of the present project is to combine the presence of (nano)antioxidant (AO) and/or (nano)antimicrobial agents (AM) with the exposure to ionizing radiation. It has been recently proven that irradiated cellulose nanocrystals exhibit peculiar antioxidant properties whose extent depends directly on the irradiation doses applied. Cellulose nanocrystals (CNCs) are nanomaterials constituted of linear homopolymer chains of β-(1→4) linked d-glucose units, generally extracted from naturally occurring cellulose sources. A very recent research [2] has evaluated the effect of the use of various radiation doses on the physicochemical structure of pristine and γ-irradiated CNCs mainly in terms of formation of new functional groups. In particular, the antioxidant capacity of irradiated CNCs has been confirmed. Specifically, an increase of γ-irradiation doses has a positive effect on the formation of new chemical functionalities, such as carboxylic and aldehydic groups, which, in combination with a decrease in the molecular weight of cellulose chains, leads to a significant improvement of antioxidant properties.

Moreover, it has also been recently proven [4] that active nanoparticles have been obtained by grafting antioxidant compounds, such as gallic acid, on CNC using ionizing radiation and it has been used for the development of antioxidant film and coating for food application.

Given the above scenario, the aim of the present project is the development of active nanocomposite polymer films obtained by embedding the irradiated and active CNCs (or other active compounds) into polyolefinic (i.e. LDPE) or biodegradable (i.e. HAVOH, chitosan) films. The presence of the developed antimicrobial or antioxidant nanoparticles into the polymer matrix will impart new functionalities to the new material and will also be used as reinforcing filler able
to improve both mechanical and barrier properties which are particularly important features for films to be used in packaging applications. Incorporating a few percent of nanoparticles in a polymeric matrix can lead to several improvements like a decrease in the package permeability to gas and aroma, and an extended shelf life for the food. Moreover, it must be taken into account that, nowadays, food processors prefer food to be irradiated in the final packaging form to prevent recontamination and to facilitate prompt shipment to market. The controlled combination of radiation technology and the use of nanomaterials can bring significant improvement and synergically contribute to worldwide food quality, quantity, and safety.

One of the objectives of the proposed research is to study the effect of ionizing radiation on packaging (nano)materials. This goal can be considered particularly challenging since the correlation between process-structure-properties of the developed materials must be determined in order to obtain high performance and high value-added nano-materials. However, food could potentially be contaminated by radylolitic products (RPs) formed in the packaging materials during the irradiation. Thus, the possible migration of the nanoparticles inside the food must be seriously taken into account. This raises a safety concern; therefore, testing packaging materials after irradiation is a fundamental part of the pre-market safety assessment of such technique.

Proposed methodology

The main objective of this 4-year research agreement project is to assess, through a systematic experimental approach, the relation between radiation processing, properties and effectiveness of emerging advanced polymer nanomaterials for possible food packaging application.

The project is organized in 5 main tasks:

Task 1: Preparation and characterization of novel nanoparticles exhibiting antimicrobial and antioxidant properties imparted by ionizing radiation. Specifically, cellulose nanocrystals will be irradiated in order to verify the formation of new chemical functionalities which can lead to improved antioxidant and antimicrobial properties. Moreover, grafting reaction with antimicrobial compounds will be also taken into account.

Task 2: Preparation and irradiation of the films and study of the effect of radiation on packaging nanomaterials. Following the indications of task 1, the research will focus on the optimization of both preparation conditions and radiation processing conditions of traditional and biodegradable
polymer films loaded with the developed active nanoparticles. The two doses that could be employed in this study should be 1 kGy and 10 kGy. The rationale for choosing these specific doses is that 1 kGy is approved by the US FDA to be used on all fresh produce in the United States for extending the shelf-life of fruits and vegetables. Given the high market value for fresh produce and since biopolymers can serve as packaging materials for fruit- and vegetable-based healthy vending machine items and for pediatric cancer patients, 1 kGy can be considered a target dose. The maximum dose that should be employed is 10 kGy because this dose limit is at the upper limit for all foods that can be treated with irradiation in the US. The decision to focus on these two critical dose points can significantly improve the chances of these research findings to be commercially exploited.

Task 3. Study of structural and functional properties of the prepared materials, in terms of morphology, physicochemical analysis, of mechanical and water and oxygen barrier properties, and effectiveness.

Task 4: Analysis of the migration of nanoparticles and radiolytic products from the packaging to the food by using food stimulants. This analysis will allow to verify safety and quality of packed foodstuffs after the irradiation procedure.

Task 5: Dissemination and exploitation. The goal of this task is twofold: to create awareness of the results among the stakeholders, food/material technologists, and consumers and to contribute to the recommendations for packaging nanomaterials for radiation processing of pre-packaged food. Indeed, a solid promotion of science-society dialogue among food technologists packaging developers and consumers is part of this research agreement proposal: it constitutes a prerequisite for a better understanding of the socio-economic, cultural and environmental dimensions of food packaging in the entire food chain.

In the first year, the following activities will be performed:

1. Literature search to define the most recent advancement on the state of art of food packaging films obtained using radiation processes and nanotechnology approach.

2. Obtainment of antioxidant nanoparticles through direct irradiation of cellulose nanocrystals and/or obtainment of antioxidant or antimicrobial cellulose nanocrystals through grafting reaction.
This activity will be performed at IZS and at IPCB and in collaboration with other partner institutions of the CRP.

3. Optimization of the processing conditions for the obtainment of antioxidant (AO) and/or antimicrobial (AM) films containing AO/AM compounds whose release can be controlled through gamma irradiation. Film will be obtained through solvent-casting technique and/or melt mixing (mixing, compression moulding, cast extrusion) or roll coating or layer by layer approach.

4. Application of ionizing radiation to the (nano)composite films. This activity will be performed at IZS and in collaboration with other partner institutions of the CRP.

5. Study of the effect of ionizing radiation on structural properties of the developed AO/AM films by means morphological analysis.

Materials

The most suitable matrices for the development of active (nano)composite materials will be chosen among (but not exclusively) the following: polylactic acid, low density polyethylene, biobased low density polyethylene, highly amorphous vinylalcohol.

Methods for film preparation

The active films will be prepared by choosing the best technique/technology among the following:

1) A melt mixing two-step process. The first step consists of melt blending LDPE or PLA or biobased LDPE or HAVOH matrix with the active nanoparticles by using an internal mixer (Thermo Scientific, Haake PolyLab QC, Karlsruhe, Germany). The melt matter is then pressed with a P300P hot press (Collin, Germany). The obtained sheets is then cut into pellets and fed into a co-rotating laboratory twin-screw extruder (Prism Eurolab 16, Thermo Electron Corporation, Stone, UK) equipped with a 10 cm-wide sheet die used to obtain the active antioxidant films.

2) Coating onto the polymeric substrates. Organic-inorganic coatings will be deposited on polymeric substrates through solvent-casting technique by using a lab-scale roll bar coater and/or through layer-by-layer technology.

Fundamental studies will be carried out to control the morphology of surface coating as well as the structural, mechanical and physical properties of the obtained materials. The activities will
consist in the dispersion of active nanoparticles into a polymeric solution and determination of suitable deposition parameters for roll-coating technique. The nano-filled materials will be analyzed by X-Rays diffractometer, SEM and TEM microscopy in order to verify the eventual presence of aggregates and to estimate the effective dispersion of the nanofillers into the polymeric coating. Contact angle measurements will be also performed in order to determine the wettability of the coated substrates. Study of thermal properties of the obtained nanocomposites will be carried out by means of thermogravimetric analysis in order to evaluate the effect of nanofillers on the thermal stability of the materials. In addition, tensile tests will be performed on the obtained films using a dynamometer in order to evaluate the influence of the presence of nanoparticles on the ultimate tensile strength and elastic modulus. Nanoindentation tests will be also performed in order to evaluate static and dynamic hardness and elastic modulus. From this analysis it will be possible to determine the effective dispersion of the nanofiller from a local mechanical response of the tested material. Tests will be also performed in order to evaluate water and oxygen permeability and sorption into the obtained nanocomposites.

**Conclusion**

In this respect, the possible expected and anticipated outcomes are listed in the following:

- Review the current status of food packaging and radiation processing techniques;

- Development of new polymer nanocomposites obtained by adding active nanoparticles, such as cellulose nanocrystals, whose antioxidant properties have been imparted through ionizing radiation and grafting reaction.

- Experimental evaluation of the effects of ionizing radiations on the properties (structural, mechanical, barrier, thermal, optical) of the selected polymer nanocomposites for food packaging application;

- Evaluation of the migration process (global and eventually specific migration tests) of nanoparticle and of radiolytic products from the films into food simulants according to the technical EU Directives;

- Contribute to expand the choice of safe materials for packaging and for pre-packaged foods intended for radiation processing.
REFERENCES


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JAPAN

DEVELOPMENT OF ORGANIC NANOWIRES VIA POLYMERIZATION IN SINGLE ION TRACKS TRIGGERED BY HIGH ENERGY PARTICLE IRRADIATION

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Introduction

Along the recent progress of nanotechnology, preparation of functional nano-objects with well-defined shape and orientation has attracted much attention. Methods to access such nano-objects are briefly categorized into bottom-up or top-down technologies. Controlled self-assembly of elaborately-designed molecules (bottom-up) gives well-defined nano-structured materials. However, it is difficult to perfectly expect how the molecules with the particular structure self-assemble into a certain nanostructure. On the other hand, top-down technology enables more general approaches, if the proper methodology is once established.

High-energy charged particles (swift heavy ions) penetrating into materials give their kinetic energy to a limited nm-sized spatial area along their trajectories, affording insoluble nanogels (nanowires) via polymerization/cross-linking reactions of the organic molecules/macromolecules. Such nanowires are isolated on the substrate by the subsequent development procedures using organic solvent and clearly visualized by conventional microscopic techniques such as atomic force microscopy (AFM) (Fig. 1). We have found that the above methodology named “Single Charged Particle-Triggered Linear Polymerization (STLiP)” is applicable to a wide variety of
polymeric materials \cite{1-11} and a certain type of small organic molecules \cite{12,13}. The noteworthy things of this method include the uniformity and controllability of nanowire length and number density by selecting the initial film thicknesses and irradiation fluences. The reactivity of the monomers and choice of solvents for the development process are the key factors to obtain nanowires in this method. So far, unsaturated C–C bond \cite{12,13} has been discovered to be useful groups for high reactivity. Since these nanowires can be obtained from many kinds of organic materials, many functional nanowires can be fabricated. For example, temperature-responsive nanowires were clearly visualized by using poly (NIPAM)-based macromolecules \cite{8,9}. Light-responsive nanowires \cite{10} and those capable of sensing application \cite{11} by means of fluorescence were reported. To the best of our knowledge, there is no general technology to obtain such nanowires (< 10 nm in diameter) from organic materials since “single” particle is the smallest unit as a tool to fabricate the materials. Here we report the recent our demonstration on the nanowire fabrication from a certain type of small molecules and their characterization methods.

Fig. 1. Schematic illustrations of nanowire fabrication processes by utilizing high-energy ion particles that trigger cross-linking/polymerization reactions along ion tracks (penumbra regions).

Experimental
Materials. Triphenylamine derivatives 1, 3, 4, and 6 were purchased from TCI Co. and used without further purification. Compounds 2 and 5, TPAmI, TPAbBr, and TPAmI were synthesized whose details were published elsewhere\cite{14}. \(^1\)H-NMR spectra were recorded in CDCl\(_3\) or acetone-\(d_6\) on a JEOL model AL-400 spectrometer, operating at 400 MHz, where chemical shifts were determined with respect to tetramethylsilane (TMS) as an internal reference. All the 9,9'-spirob[9H-fluorene](SBF) derivatives were purchased from Tokyo Chemical Industry Co. and used as-received.

Nanowire Fabrication and Observation. Si substrates were cut into 1.5 cm\(^2\) square pieces and sonicated in 2-propanol and dried. The quartz substrates used had 1 mm thickness and dimensions 9 × 40 mm. All the substrates were exposed to UV-O\(_3\) to clean the surface prior to use. All the SBF derivatives were dissolved in CHCl\(_3\) and dropcast or spincoated onto the substrates to yield thin films. The thickness of the films was set at 100−500 nm, as confirmed by a Veeco Instruments Inc. Dektak 150 surface profiler. As a high-energy particle source, 490 MeV \(^{192}\)Os\(^{30+}\) or 350 MeV \(^{129}\)Xe\(^{26+}\) ions were generated from a cyclotron accelerator at Takasaki Advanced Radiation Research Institute. 150 MeV \(^{107}\)Ag\(^{11+}\), 100 MeV \(^{58}\)Ni\(^{7+}\), and 60 MeV \(^{28}\)Si\(^{5+}\), and 60 MeV \(^{16}\)O\(^{5+}\) MeV were generated from a pelletron accelerator at Inter University Accelerator Centre. All the thin films were evacuated (< 1 × 10\(^{-4}\) Pa), and high-energy particles were irradiated orthogonally to the film surfaces at the fluence of 1 × 10\(^9\)−5 × 10\(^{11}\) cm\(^{-2}\). No sublimation under vacuum was confirmed based on the film thickness. After irradiation, the films were immersed in toluene for ~1 min at room temperature. The morphologies of the nanowires were determined by using a Bruker Co. Multimode 8 atomic force microscope (AFM).

Simulation of High-Energy Particle Irradiation. The loss of the kinetic energy of the ions due to their traversal through the organic films (linear energy transfer; LET) was estimated using the Monte-Carlo code (SRIM 2008) based on the differential cross-section of the particle in a matter based on the densities of the target materials presumed from their crystalline structures, if available. The film thickness was set at 10 µm (larger than the actual maximum film thickness). The density of the film was set at 1.25,\(^{15}\) 1.48, 1.63,\(^{16}\) 1.84,\(^{17}\) 1.34,\(^{18}\) and 1.24\(^{19}\) g cm\(^{-1}\) for SBF, \(2\)Br\((4\)Br\))-SBF, \(2,2'\)Br\(2(2,7\)Br\(_2\))-SBF, Br\(_4\)-SBF, SBF\(_2\), and SBF\(_3\), respectively. The \(^{129}\)Xe particle was irradiated 1000 times.
X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectra were measured on a SHIMADZU ESCA-3400 electron spectrometer. Bundled nanowires were obtained by 350 MeV $^{129}$Xe$^{26+}$ irradiation at the fluence of $1.0–5.0 \times 10^{11}$ cm$^{-2}$ on the silicon substrate and the system evacuated ($< 1 \times 10^{-5}$ Pa) prior to the measurements with the bulk films as the references.

Results and Discussion


Triphenyl amines are known to undergo dimerization reaction when oxidized to give radical cation species $^{[21,22]}$. It is considered that aromatic amine compounds provide radical species upon irradiation and efficient propagation reactions in the solid state. Compounds 1–6 with different molecular sizes were prepared in the present work (Fig. 2a), and their thin films were prepared on Si substrates by conventional spin-coating or dropcast methods. Ion-beam irradiation of the prepared films at the low fluence ($\sim 10^8–10^{10}$ cm$^{-2}$) hopefully results in propagation reactions, leading to the formation of one-dimensional organogels along the trajectories of the respective particles that is often called ion tracks. Because of the large difference between the linear energy transfers (LETs) of organic materials and the Si wafer, the primary charged particles and secondary electrons preferentially induce the formation of dense reactive species at the pentacene/Si interface, leading to the heterogeneous covalent-bond formation. Thus, the termini of the obtained nanowires become covalently bound to the surface of the Si wafer via Si–C or Si–O–C bonds, preventing the nanowires from easily being washed away by solvents. The crucial requisite for this technique, named as “single particle-triggered linear polymerization (STLiP)”, is the remarkable difference in solubility between irradiated and non-irradiated parts, which enable the easy isolation of the resultant nanowires by development solvents. In principle, the initially formed nanowires stand on a substrate, where the length of the nanowires corresponds to the thickness of the films. Nevertheless, due to the interfacial surface tensions by organic solvent, observed nanowires usually lie down to the substrate.

When the aromatic amine films were exposed to 490 MeV $^{192}$Os$^{30+}$ particles (LET $\sim 13800$ eV nm$^{-1}$) at the low fluence followed by the development in hexane or toluene, nanowire objects consisting of aromatic derivatives were visualized in AFM except the compound 1 (Fig. 2). We consider that small molecular size of 1 caused a difficulty in polymerizing into high molecular-
weight products upon radical generation and only gave, if any, fragile nanowires that is easily washed away during development. By carefully looking at the images for 2–6, partial fragmentation of the nanowires was confirmed, implying the bond-break or loose of the polymerized products. Nevertheless, even for the thick (> 1 μm) films prepared by drop-cast method, obvious nanowires with ultrahigh aspect ratio were observed. Compared to our previous reports based on polymer materials, the obtained nanowires appeared flexible, while their diameters appeared small. Most likely due to the flexibility, entangled, bundled, and networked structures of nanowires were formed. Moreover, cross-sectional profiles in AFM revealed the remarkable uniformity of nanowire diameters that is characterized by the single particle-triggered intra-track reactions. For example, when scanning along the dotted line drawn in Fig. 2d, we can visualize the height that well agrees well with the single nanowire as well as overlapped two or three nanowires (Fig. 2h).

In order to find some evidence that the nanowires were dominantly formed through not crosslinking but polymerization, we studied the effect of solvents for development on the nanowire isolation. For example, solvent-dependence was demonstrated for 2. Firstly, development with \textit{n}-hexane afforded the networked nanowires (Fig. 3a). The dispersed radius distribution of 5.2±0.6 nm (Fig. 3b) indicated that non-developed small oligomers and monomers remained. Further development with toluene did not strongly affect the AFM images (Fig. 3c) but the averaged diameter of nanowires got decreased (Fig. 3d), suggesting the removal of the small oligomers and monomers. However, at the same time, dissociation of polymeric products took place when immersing the nanowires into high solubility solvents. In fact, wavy and thin nanowires with considerable fragmentation were observed after further development with CHCl₃ (Fig. 3e). In this case, the averaged radius became increased with dispersed distribution (Fig. 3f). We interpreted this phenomenon as a consequence of dissociation of polymeric products by dissolution in solvent, which resulted in the observation of nanowires composed of loosely bound polymeric products.
Fig. 2. (a) Chemical structures of aromatic amines 1–6. (b) AFM topographic images of nanowires from dropcast films of (b) 1, (c) 2, (d) 3, (e) 4, (f) 5, and (g) 6. The films were irradiated with 490 MeV $^{192}$Os$^{30+}$ particles at the fluence of $1.0 \times 10^9$ and $2.0 \times 10^8$ ions cm$^{-2}$ for (b–e, g) and (f), respectively, and developed with $n$-hexane at r.t. for 1 and 60 °C for 2 and 4–6, and $n$-hexane followed by toluene at r.t. for 3. Scale bars represent 500 nm. (h) Cross-sectional profile along dotted line in (d).

Fig. 3. (a, c, e) AFM topographic images and (b, d, f) their radius distributions of nanowires from a dropcast film of 2 isolated via sequential development. The film was irradiated with 490 MeV $^{192}$Os$^{30+}$ particles at the fluence of $1.0 \times 10^{11}$ cm$^{-2}$ and developed by (a, b) $n$-hexane, followed by (c, d) toluene and then (e, f) CHCl$_3$ at r.t. Scale bars represent 500 nm.

2. Gel permeation chromatography (GPC) analysis and electronic spin resonance (ESR) measurements: Study with halogenated triphenylamine nanowires $^{[14]}$

The polymerized products by STLip were investigated by size-exclusion chromatography (SEC) analysis. The formation of nanowires was confirmed by AFM after irradiation with 490 MeV $^{192}$Os$^{30+}$ at a fluence of $1.0 \times 10^{11}$ ions cm$^{-2}$ and subsequent development of the dropcast films of each compound. The THF extract was obtained by sonication of the nanowires on the substrates and the following filtration through a PTFE membrane, and injected into the SEC system using
THF as the eluent. The broad peaks with large excluded volume were appeared in the SEC charts of all TPs, indicating the presence of polymerized products (Fig. 4b, d, f). On the other hand, the irradiated films without development were analyzed by electron paramagnetic resonance (EPR) method to detect the residual neutral radical species. It is recognized that residual stable radical species were still present even after 490 MeV $^{192}$Os$^{30+}$ ion irradiation and subsequent exposure to air (Fig. 5). The radical species appeared in TPA$_{Br}$ (Fig. S7c) after irradiation showed an EPR signal with a $g$ value of 2.002, which indicates the presence of not bromine but organic radicals in nanowires. The amount of spin density for the residue seems to be much higher in TPA$_{Br}$ than in TPA$_{H}$. However, due to the broad and small peaks, quantitative discussion may mislead the reaction efficiency in the system. Through SEC and EPR studies, it is probable to describe that organic radical species generated upon the high-energy particle irradiation induced polymerization reactions and those polymers are assembled to form wire-shaped insoluble nanogels.

![Fig. 4. AFM topographic images of nanowires from dropcast films of (a) TPA$_{H}$, (c) TPA$_{Br}$ and (e) TPA$_{I}$. The film thickness is 4.0, 2.5, and 4.0 µm for TPA$_{H}$, TPA$_{Br}$, and TPA$_{I}$, respectively. The films were irradiated with 490 MeV $^{192}$Os$^{30+}$ particles at the fluence of 1.0 × 10$^9$ ions cm$^{-2}$ and developed with cyclohexane. Scale bars represent 500 nm. (d–f) Analytical SEC profiles of monomers (red) and soluble fractions of their nanowires (blue) in THF for (d) TPA$_{H}$, (e) TPA$_{Br}$ and (f) TPA$_{I}$. Retention time was monitored at 310 nm light.](image)

![Fig. 5. EPR spectra of solid state (a)(d) TPA$_{H}$, (b)(e) TPA$_{Br}$ and (c)(f) TPA$_{I}$. Samples in (a)–(c) were as-synthesized solids. Samples in (d)–(f) were after irradiation with 490 MeV $^{192}$Os$^{30+}$ particles at a fluence of 1 × 10$^{10}$ ions cm$^{-2}$. No development process was carried out. Asterisk indicates signals from](image)
Mn$^{2+}$ as an internal standard. The sample weight was (a) 1.23, (b) 2.68, (c) 1.29, (d) 1.27, (e) 2.67, and (g) 1.29 mg.


The chemical structures of SBF, 2Br-SBF, 2,2′Br$_2$-SBF, Br$_4$-SBF, SBF$_2$, and SBF$_3$ are shown in Fig. 6a. To demonstrate the applicability of STLiP, the thin films of the SBF derivatives were exposed to 350 MeV $^{129}$Xe$^{26+}$ ions at the fluence of $1 \times 10^{10}$ cm$^{-2}$ under vacuum, followed by development with toluene. After development, the morphology, shape, and size were studied by AFM. As clearly shown in Fig. 6b, SBF yielded clear nanowires with uniform diameters, and similar results were obtained by all the other SBF derivatives used. The uniform size of the nanowires was unchanged over a variety of development conditions including CHCl$_3$ for 1 h. No obvious fragmentation was observed, suggesting that the SBFs are interconnected in the nanowires. The unchanged morphology of the pattern is typical of cross-linked negative resist materials and suggests the gelation of the polymerized SBFs in the present nanowires. The nanowire cross-sectional radius was examined by AFM. In the height profiles of an individual nanowire, the half-width ($r_w$) and half-height ($r_h$) of the cross-section of the nanowires were evaluated. By applying the ellipsoidal model, the nanowire radius ($r_{NW}$) was estimated as $r_{NW} = (r_wr_h)^{1/2}$. Fig. 6c shows the distribution of the radii of 30 nanowires from SBF as observed in the microscopic frame of each compound.

Fig. 6. (a) Chemical structures of SBF derivatives. (b) AFM image of nanowires from SBF. The films were irradiated by 350 MeV $^{129}$Xe$^{26+}$ particles at a fluence of $1.0 \times 10^{10}$ cm$^{-2}$ and developed by toluene at room temperature. Scale bars represent 500 nm. (c) Radius ($r_{NW}$) distributions and average radius of nanowires from dropcast films of SBF.
The cross-sectional radii of the nanowires are correlated with the efficiency of the polymerization/crosslinking reaction. As shown in Table 1, the increasing order of radii was revealed as \( r(\text{SBF}) < r(2\text{Br-SBF}) < r(2,2'\text{Br}_2\text{-SBF}) < r(\text{Br}_4\text{-SBF}) \) and \( r(\text{SBF}_2) < r(\text{SBF}_3) \). We presumed that the larger \( r \) observed in Br-substituted SBFs is due to the highly efficient bond-formation reactions, including the dissociative electron attachment of the generated secondary electrons to the halogenated compounds [24–26]. The order of non-halogenated SBFs can be interpreted in terms of the effect of molecular size on the oligomerization/crosslinking reactions; the starting larger oligomers reach the polymerized products more easily. However, the difference between \( r(\text{SBF}_3) \) and \( r(\text{SBF}_3) \) was small, indicating this effect is saturated at a certain size of the molecules with similar reactive sites. The other important finding is the narrow distribution of the nanowire radii compared with those produced from polymer films [1–11]. A possible reason is the much smaller molecular volumes of the SBF derivatives compared to those of the polymer chains with polydispersity. The sharp threshold of reaction efficiency, corresponding to \( r \), is considered to appear due to this reason.

In the STL iP method, the cross-sectional radii of the nanowires should be related to the initiation/propagation efficiency of the monomer molecules triggered by the given energy of the incident high-energy particles. The intra-track radial energy density, defined in terms of the collision of incident particles with target materials, is mainly classified into two regions—the “core” and “penumbra.” [27–30] The “core” is a narrow central circular zone with a radius of a few nanometers, where extremely high energy deposition occurs, dominated by the knock-on collision processes between the incident particles and the atoms of the target material. The deposited energy is mainly associated with the process of plasma oscillation of the electrons ejected due to primary ionizations, as well as direct electronic excitation.

The size of the core is defined as the spatial region of plasma oscillations induced by the interactions between a high-energy charged particle and the target material, assuming uniform electron density (\( n \)) in the material. The plasma oscillation frequency (\( \Omega \)) is given by

\[
\Omega = \left(\frac{ne^2}{me_0}\right)^{1/2},
\]

where \( m \) and \( e_0 \) denote the mass of the electron and the permittivity of free space, respectively.

For example, SBF has a density of \( \sim 1.25 \times 10^3 \) kg m\(^{-3}\) and the number of electrons in the outermost
shell of SBF is 116. Based on these parameters, the value of $\Omega$ is calculated as $2.96 \times 10^{16}$ s$^{-1}$. The energy of all the incident charged particles ($E$) employed is in the range of non-relativity. Thus, the velocity ($v$) of the particle is given by the following equation.

$$E \cdot e = \frac{1}{2} m_p v^2,$$

(3)

where $m_p$ is the mass of the incident particle. The calculated $v$ of $2.28 \times 10^7$ m s$^{-1}$ for 350 MeV $^{129}$Xe particle is confirmed to be under 10% of $c$ (the speed of light). In contrast, the value of $v$ is larger than the Bohr orbital velocity, suggesting that the Xe particles are swift heavy ions whose energy loss process is mainly dominated by inelastic scattering with ionization. As a result, $r_c$ is given in terms of $\Omega$ and $v$ as

$$r_c = \frac{v}{\Omega}.$$  

(4)

The value of $r_c$ is estimated as 0.75–0.83 nm for the SBF derivatives (Table 1), which is much smaller than the observed nanowire radii. This is suggestive of the crucial role of radial-energy density in the penumbra region, rather than the density in the core region, in determining nanowire radii.

The “penumbra” is a peripheral zone with radius ranging from nanometers to micrometers, where energy deposition occurs mainly through ionization events caused by energetic secondary electrons ($\delta$-rays) released by the incident charged particle from the center of the “core.” The energy spectra of the generated $\delta$-rays are theoretically predictable [29,30]. The maximum radial range values, $r_p$, summarized in Table 1, are based on the densities of the SBF derivatives used.

The radial energy distribution in the penumbra region ($\rho_p (r)$) follows the inverse square rule and is described by the following equation [31].

$$\rho_p (r) = \frac{LET}{2\pi r^2} \left\{ 1 + 2 \cdot \ln \left( \frac{r_p}{r_c} \right) \right\},$$

(5)

where the LET values are almost constant for each depth. Based on eq. 5, the energy density at the surface of the nanowires, $\rho_s$, is calculated by using the radius of each nanowire, and has been summarized in Table 1. The given energy per molecule around the nanowire surface is also
summarized in Table 1, calculated from $\rho_s$ and molecular volumes, which are in turn estimated from the crystal structures of the SBF derivatives [15–19]. At the nanowire surface, at least one chemical bond is likely formed to immobilize the molecule. One SBF molecule is surrounded by six nearest neighbor molecules capable of bond formation based on the reported crystal structures, and the SBF molecule should react with either of the three inner molecules to be immobilized to a nanowire. The $G$ values for bond formation with the inner nearest neighbors are roughly estimated to be in the range of 8.6–9.7 (100 eV)$^{-1}$ for the monomeric SBF derivatives upon 350 MeV $^{129}$Xe particle irradiation, whereas the dimer and trimer yielded smaller $G$ values of 5.4 and 3.9 (100 eV)$^{-1}$, respectively. These values are larger than that for the case of the polymer, revealing efficient solid-state polymerization of the SBF derivatives upon high-energy particle irradiation. The lower values observed for oligomeric SBF$_2$ and SBF$_3$ can be interpreted as a hypothesis that a larger molecular volume can result in nanowires with a smaller reaction efficiency. Since brominated SBFs afford larger $r$ values but reveal similar $G$ values with non-brominated SBF along the radial distance of their nanowire surfaces, it is clear that bromination of the SBF rings resulted in higher efficiencies of the polymerization reactions. Note that the high electron density on the Br atoms has already been taken into account for the value of deposited energy density.

### Table 1. Summary of Density, Calculated Maximum Radial Range $R_C$ and $R_p$, Calculated Linear Energy Transfer (LET), Radii in Nanowire Form $R_{NW}$, Calculated Energy Density at the Nanowire Radii $\rho_s$, Estimated Molecular Volume $V_{molecule}$, Given Energy Per Molecule by High-Energy Ions $E_{molecule}$, and Estimated $G$ for SBF, 2Br-SBF, 2,2′Br-SBF, Br$_4$-SBF, SBF$_2$, and SBF$_3$ Upon Irradiation with 350 MeV $^{129}$Xe$^{26+}$

<table>
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<th></th>
<th>Density / g cm$^{-3}$</th>
<th>LET / eV nm$^{-1}$</th>
<th>$r_c$ / nm</th>
<th>$r_p$ / nm</th>
<th>$r_{NW}$ / nm</th>
<th>$\rho_s$ / eV nm$^{-3}$</th>
<th>$V_{molecule}$ / nm$^3$</th>
<th>$E_{molecule}$ / eV</th>
<th>$G$ value / (100 eV)$^{-1}$</th>
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<td>0.77</td>
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</tbody>
</table>

The chemical reactions triggered by high-energy charged particles were investigated by XPS. Photoelectrons were detected in both the film and nanowires, as exemplified for 2Br-SBF and (c,d) Br₄-SBF (Fig. 7). We focused on the electrons of the C 1s and Br 3d orbitals and compared the ratio of their intensities for the starting film and the isolated nanowires. Non-irradiated films yielded peak intensity ratios of about 0.11, 0.24, and 0.48 for Br-SBFs, Br₂-SBFs, and Br₄-SBF, respectively, which explains well the bromine contents of the compounds. Table 2 summarizes the observed peak area ratios of (Br 3d)/(C 1s). It was revealed that the ratios for the nanowires were almost 50% those of the non-irradiated films in the case of 2Br-SBF (almost identical in the case with 4Br-SBF). Notably, the ratio drastically dropped off for the nanowires of 2,2′Br₂-SBF (2,7Br₂-SBF also), revealing about 20% of the peak intensity ratio of (Br 3d)/(C 1s). In the case of Br₄-SBF, about 20% of the peak ratio was recorded, suggesting that non-negligible numbers of Br atoms were dissociated and escaped from the wires as HBr, Br₂, or other small molecular weight bromine compounds during the irradiation or development process. The Br atoms were actually detached from the SBF cores efficiently removed by swift heavy ion irradiation, which generated the reactive species efficiently to form new covalent bonds. This is reasonable considering the lower bond energy of C₆H₅–Br (~336 kJ mol⁻¹) compared to that of C₆H₅–H (~472 kJ mol⁻¹) [32].
Fig. 7. (a,c) C 1s and (b,d) Br 3d X-ray photoelectron spectra for non-irradiated films (gray) and nanowires (black) fabricated from (a,b) \textit{2Br-SBF} and (c,d) \textit{Br}_4\textit{-SBF}. Dotted lines represent baselines for films (gray) and nanowires (black).

**TABLE 2.** SUMMARY OF OBSERVED SIGNAL INTENSITY RATIO OF (BR 3D)/(C 1S) IN X-RAY PHOTOELECTRON SPECTRA FOR FILMS AND NANOWIRES.

<table>
<thead>
<tr>
<th></th>
<th>Film</th>
<th>Nanowire</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Br-SBF</td>
<td>0.11</td>
<td>0.056</td>
</tr>
<tr>
<td>2,2’Br_2-SBF</td>
<td>0.23</td>
<td>0.046</td>
</tr>
<tr>
<td>Br_4-SBF</td>
<td>0.48</td>
<td>0.094</td>
</tr>
</tbody>
</table>

**Conclusion**

We demonstrated a unique technique “Single Particle-Triggered Linear Polymerization (STLiP)” in the solid state, where high-energy ions deposit energy along their trajectories to generate active radicals for propagation reactions. The polymerized products were integrated into nanowires that were isolated via development with appropriate organic solvents. By means of stepwise developments, we indirectly but certainly proved that the driving force for nanowire formation was not only crosslinking but also polymerization. It is revealed that halogenation (Cl, Br, and I) of aromatic structures serves as an effective design strategy for nanowire fabrication by the STLiP method. The preferential dissociation of C–Br bonds toward C–H ones upon irradiation was confirmed by the XPS measurements. The $G$ values at the surface of nanowires were estimated by using the molecular packing information from the single crystal structures, radii of the nanowires, and simulated LET values.

The outcomes of our research would be the development of nanowire-networks with extralarge specific surface area, unprecedented organic standing nanowire arrays, nano-sized polymer matrices with ultrahigh aspect ratio. These three features are beneficial for sensing, optical/electronic, and biological applications, respectively.

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• IUAC, India – Drs. Devesh Kumar Avasthi, GBVS Lakshmi

REFERENCES

Abstract
This study focuses on track membranes and their application in various areas of materials science. The results of the study of chemical (electroless) template synthesis of metal nanostructures of the copper subgroup in channels of track membranes based on polyethylene terephthalate, as well as the practical application of the obtained composite membranes in catalysis are presented. This report demonstrates the effectiveness of composite catalysts based on copper, silver and gold nanotubes on the example of p-nitrophenol reduction, decomposition of hydrogen peroxide and the reaction of aminomethylation of acetophenone. The report concludes with a brief abstract of the project entitled "Radiation induced and template synthesis of the photocatalytically active ion-track membrane composites", identifies the main tasks and areas of the project.

1. BACKGROUND

Track-etched membranes (TeMs) are a high-tech product of modern nanotechnology, they are thin polymer films with through pores of various geometries made by irradiating a thin polymer film with accelerated ions, characterized by high uniformity of pores in size, structure and their distribution [1, 2]. On an industrial scale, TeMs are produced on the basis of a limited number of polymers: most often they use polyethylene terephthalate (PET) or polycarbonate (PC), whose surface properties do not always correspond to the necessary for their universal use in various fields. A number of important operational parameters of membrane processes (such as selectivity, productivity, possibility of regeneration, etc.) are significantly determined by the colloid-chemical properties of the membrane pore surface and, particularly, by the degree of its hydrophilicity or hydrophobicity [3].

For quite a long time, the scope of application of TeMs was limited only to water purification. At present, all over the world, methods of cleaning using TM are no longer in doubt about their
effectiveness and competitiveness. They provide precision microfiltration of liquids and gases, in membrane distillation and direct osmosis, are used for blood purification, in biotechnology, pharmacology, chemistry, microelectronics and other fields of science and production [4]. TeMs are not only unique filtration materials, but can also serve as matrices for the preparation of ordered arrays of metallic micro and nanostructures (NSs) with unique physical properties [5]. A distinctive feature of template synthesis using TM as template matrices is the ability to control the properties of nanomaterials created through the use of templates with a given shape and pore size [6]. A wide range of classes of materials deposited in the TeM pores, a sufficient range of deposition techniques, and undoubtedly immense prospects for using the resulting ordered arrays of nanostructures (in case of removing a template) or composite membranes (nanotubes/nanowires in a membrane matrix). All this determines the relevance and significance of given studies.

The DC-60 accelerator complex is one of the leading nuclear physics centers in Kazakhstan for conducting both fundamental and applied research in the field of nuclear physics, engineering, chemistry, and nanotechnology [7]. One of the accelerator channels is technological and designed specifically for the irradiation of a polymer film on an industrial scale. The technological parameters of DC-60 allow obtaining membranes with precisely defined channel sizes from 0.03 μm to 10 μm, with density from 1×10⁵ to 1×10⁹ pores/cm².

For the irradiation of the polymer film on the DC-60 cyclotron, ⁸⁴Kr and ¹³²Xe ions with energy of 1.75 MeV/nucleon are used, which provide specific energy losses of the dE/dx ion beam at the level of 6÷10 MeV/μm. Using the SRIM program (Table 1), the total ranges of krypton and xenon ions, the specific energy losses due to the interaction with the electron shell and the nuclear interaction of ions and film atoms were calculated [8].

**TABLE 1 - ENERGY LOSS AND THE TOTAL RANGE OF KRYPTON ⁸⁴KR AND XENON ¹³²XE IONS IN PET FILM**

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Ion energy MeV/nucleon</th>
<th>dE/dx electr, MeV</th>
<th>dE/dx nucl, keV/μm</th>
<th>Full path, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁸⁴Kr</td>
<td>1</td>
<td>7.613E+03</td>
<td>2.398E+01</td>
<td>18.32</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>7.632E+03</td>
<td>1.708E+01</td>
<td>23.79</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>7.567E+03</td>
<td>1.500E+01</td>
<td>26.55</td>
</tr>
</tbody>
</table>
SEM images of lateral chips of PET TeMs with various pore densities are shown in Fig. 1.

<table>
<thead>
<tr>
<th>132Xe</th>
<th>1</th>
<th>132</th>
<th>1.118E+04</th>
<th>5.015E+01</th>
<th>20.70</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5</td>
<td>198</td>
<td>1.185E+04</td>
<td>3.590E+01</td>
<td>26.38</td>
</tr>
<tr>
<td></td>
<td>1.75</td>
<td>231</td>
<td>1.200E+04</td>
<td>3.158E+01</td>
<td>29.14</td>
</tr>
</tbody>
</table>

Varying the conditions of chemical etching allows obtaining tracks of various geometries: conical, hourglass, bottle-shaped, which in turn opens up significant prospects for the use of such asymmetric membranes, whose properties are different from isotropic tracks [9, 10].

Since 1991, the work of Chakarvarti and Vetther [11], in which it was reported about obtaining microstructures in porous templates using the technique of electrochemical deposition, similarly deposited a variety of mono- and multicomponent metallic nanostructures that have found practical application in microelectronics, nanosensorics, materials science and medicine. It should be noted that for the electrochemical synthesis of the wires of nano- and submicron diameter with a length within the thickness of used TM, it is necessary to form a center of nucleation of galvanic residue directly in channels of membrane, on one of its surfaces, which is achieved by vacuum deposition of 10-50 nm metal layer on membrane surface (Au, Pt, Pd) [12]. If, in electrochemical treatment of metals method, electrons required for the recovery of metal ions are delivered by external current sources, then in the chemical deposition method (electroless deposition), the necessary electrons are provided by catalytic oxidation of the reducing agent. This method involves the use of a chemical reducing agent to deposite material from the solution onto the template surface and consists of three successive stages: sensitization, activation, and, directly, deposition [13, 14].
At the stage of sensitization (sensitivity increase), the membranes are processed in a solution containing \( \text{SnCl}_2 \)-25 g/l and \( \text{HCl} \) (37%) -60 g/l, the TeM sample is immersed in this solution for 30 minutes, then within a few minutes the sample is washed under running water. When washing with water, tin salts hydrolyze and quite significant amounts (up to 10 mmol/m\(^2\)) of poorly soluble hydrolysis products are deposited on the surface, forming a continuous layer of thickness several hundred nanometers. The surface becomes hydrophilic and capable of binding ions of noble catalytically active metals, restoring them or forming poorly soluble compounds that are attached to the sensitized surface (from 0.5 to 10 of milligrams per 1 m\(^2\)). The activation of the template consists in the treatment of sensitized surface with solutions of compounds from catalytically active metals: \( \text{Pd, Pt, Ag, Au, Rh, Ru, Os, Ir} \). In order to deposit the silver, a sensitization stage is sufficient, since then the reaction proceeds in an autocatalytic mode [15,16].

**Deposition.** Solutions for the production of chemical coatings in the simplest case contain a metal salt and a reducing agent. However, such solutions are unstable, and metal ions are reduced to form a metallic deposit in the entire volume of the solution. At the initial time, the reaction of interaction of metal ions with a reducing agent is non-catalytic, but as the metal particles are formed, the reaction takes on a catalytic character, and its rate increases with increasing surface of the deposition.

To stabilize the solution, it is injected by the following:

- complexing substances (ligands), which provide the formation of strong complexes with metal ions [17]. With an increase in complex strength, the interaction reaction rate of metal ions with a reducing agent decreases;
- substances that create a certain pH value (alkalis or acids, buffering additives);
- stabilizers are special substances that in low concentrations (1-100 mg/l) significantly increase the solution stability [18].

The main feature of chemical deposition process is that the deposition of material begins with pores walls. Unlike electrochemical deposition, where the size of metallic nanowires is controlled, in the technique of chemical deposition, the width of nanostructures is equal to the width of membrane track, and the length of resulting nanostructures is equivalent to the thickness of the matrix used [19].

**2. MATERIALS AND METHODS**
POLYMER TEMPLATE PREPARATION AND TREATMENT
TeMs were prepared from 12.0 µm PET film by irradiation with $^{84}$Kr ions (energy = 1.75 MeV per nucleon, fluence = $4 \times 10^7$ ions/cm$^2$ and $1 \times 10^9$) at the DC-60 heavy ion accelerator in Astana, Kazakhstan. Subsequently, the irradiated film was etched in 2.2 M NaOH solution at 85 ± 1°C. The pore size did not exceed 380 ± 10 nm and 110± 5 nm for films with a pores density of $4 \times 10^7$ and $1 \times 10^9$ respectively.

For increasing of COOH- groups concentration, PET TeM samples were oxidized in H$_2$O$_2$/UV system. Details of the method were described elsewhere [20].

ELECTROLESS PLATING
Prior to electroless deposition of metals, the PET template was exposed to activation and sensitization procedures according to procedure described in [21] for copper plating. For Au, Ag and Ag/Au composites a deposition technique was detailed in our previous papers [22].

COMPOSITES CHARACTERIZATION
The thickness of the Cu NT walls was determined from the difference in the diameters of the pristine PET TeMs and the sample after deposition using the Hagen-Poiseuille equation.

Detailed structural and compositional studies were carried out using a scanning electron microscope (SEM) JEOL JFC-7500F and Hitachi TeM3030 instrument equipped with a Bruker XFlash MIN SVE microanalysis system.

X-ray diffraction (XRD) measurements of the “as-prepared” composite membrane samples were obtained on a D8 Advance (Bruker, Germany). X-ray was generated at 40 mA and 40 kV and the scanning position ranged from 15-90° 2(θ). The crystal grain sizes were calculated using Scherrer equation.

CATALYSIS
THE REDUCTION OF 4-NITROPHENOL (4-NP) TO 4-AMINOPHENOL (4-AP)
A sample of composite membrane size of 2×2 cm (Cu NTs) and 5×5 cm (Ag/PET, Au/PET and Au/Ag/PET) was immersed into the stirred reaction mixture of 10 ml of 7.82·10$^{-6}$ M 4-NP and the 7.82·10$^{-3}$ M NaBH$_4$ aqueous solution. The reaction rate was monitored at the temperature of
25±0.1 °C every 5 min using UV-Vis spectrophotometer. All samples of the composites were tested at least 5 times, after each run the catalyst was washed in deionized water, dried and used further without any additional purification or activation treatment. The catalytic ability was also evaluated in the temperature range of 16-40 °C and the activation energy was calculated based on the Arrhenius plot.

HYDROGEN PEROXIDE DECOMPOSITION REACTION

The decomposition of H$_2$O$_2$ was conducted under permanent stirring in a temperature range of 25–45°C [23]. A 5.75×4.25 cm composite sample was placed in a 250-mL thermostatted reaction vessel; after the addition of 50 mL of 1.02 wt % hydrogen peroxide preliminarily held at the reaction temperature for 30 min, the system was tightly sealed. The H$_2$O$_2$ working solution concentration was determined by standardization against a KMnO$_4$ solution; the reaction rate constant was determined via measuring the volume of oxygen released at various time intervals from the onset of the reaction.

MANNICH REACTION

Examination of the catalytic properties of composites in the Mannich reaction was carried out according to [24]. Benzaldehyde (1 mmol), aniline (1 mmol) and acetophenone (1 mmol) in methanol (5 ml) were stirred in a nitrogen atmosphere at room temperature in the presence of 2×2 cm sample of composite membrane (mass of loaded Cu NTs – 3.9±0.1 mg or 1.96 mol%). Completion of the reaction was monitored by TLC (eluent Petroleum Ether/AcOEt = 80:20), afterward the solid product was filtered and washed with methanol. The solvent was removed under reduced pressure and the final product was recrystallized from EtOH.

3. RESULTS AND DISCUSSION

We have carried out several studies on features of chemical template synthesis of nanotubes based on metals of the copper subgroup (copper, silver, gold), and also studied their catalytic activity using several reactions as an example.

P-NITROPHENOL REDUCTION REACTION
Using the example of the reaction of liquid phase reduction of p-nitrophenol, widely used for the primary screening of nanoscale catalysts, we studied the influence of various factors on catalytic properties of composite track membranes with copper metal subgroup nanotubes: density and pore size, deposition conditions (composition of activation solution [25], temperature, duration, effect of pretreatment conditions). We chemically deposited NTs on the basis of Ag, Au and Ag/Au mixed composition (pore density of PET template $1 \times 10^9$ ion/cm$^2$), as well as copper NTs (pore density of PET template $4 \times 10^7$ ion/cm$^2$) [26].

The catalytic reduction reaction of 4-NP in the presence of nanoscale catalysts has a pseudo-first order under the condition of an excess of reducing agent (NaBH$_4$), which allows investigating the reaction kinetics by changing the amount of initial reagent [27]. In the absence of catalysts, the formation of final product 4-AP was not observed even with an increase in the reaction time to 120 hours. Table 2 shows the structural data of the synthesized NTs, as well as the change in the kinetic parameters of the 4-NP reduction reaction. As can be seen from the presented data, the composite of Ag/Au/PET mixed composition due to the synergistic effect of silver and gold shows a higher catalytic activity than monometallic composites [22]. Also, for all three types of synthesized composites, with an increase in the deposition time to 24 hours, a decrease in the catalytic activity is observed. That is due to the enlargement of the crystallite size on the surface of composite and inside nanotubes. It is important to note that the activity of composites, which were tested without any regeneration and activation procedures, slightly decreases during 5 consecutive testing cycles.

### TABLE 2 - CHANGES IN THE CATALYTIC ACTIVITY OF COMPOSITE MEMBRANES DEPENDING ON DEPOSITION DURATION

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NTs embedded in PET membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au</td>
</tr>
<tr>
<td>Pore density of PET template, nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^9$</td>
</tr>
<tr>
<td>Pore diameter of PET template, nm</td>
<td></td>
</tr>
</tbody>
</table>
The Au/PET composite has a non-linear dependence of the rate constant from temperature. The rate constant increases linearly in the temperature range 19–35°C (in this temperature range, \(E_a=65.32\, \text{kJ/mol}\)). With a further increase in temperature, the rate constant decreases significantly and the activation energy in this region is negative and equals \(-91.44\, \text{kJ/mol}\) \[28\]. It was found that this phenomenon is due to structural changes in Au/PET samples themselves, particularly, changes in the size of gold nanoparticles on surface and in channels of composite membrane due to leaching of the active gold nanoparticles with the smallest diameter from composite membrane surface, since the reaction is carried out with vigorous stirring \[29\].

In \[30, 31\] PET TM template used for the deposition of palladium nanoparticles was previously subjected to oxidation in potassium permanganate sulphate and amination. As a result of polymer template modification, samples of composite membranes showed much higher efficiency during separation of hydrogen and \(\text{CO}_2\). Therefore, by varying the functional properties of initial templates, nanomaterials can be obtained with given structural parameters and properties. A significant improvement in catalytic properties of composite track membranes with gold nanotubes was achieved through preliminary oxidative modification of the polymer template \[32\], and the rate constant of decomposition of p-NP decomposition was 23% higher than in the case of using the “normal” etched PET membrane. This improvement in catalytic activity is due to an increase in the concentration of terminal carboxyl groups on PET template surface, which in turn leads to
an increase in the number of active nucleation sites at the stage of template activation. Similar results were achieved by us in the case of composite NT copper membranes. In the case of copper NT, we also established a direct dependence of catalytic activity from the temperature of copper chemical deposition [33]. The structure of samples synthesized in the temperature range 3–40°C, as well as dynamics of the change in rate constant of 4-NP reduction reaction for 6 test cycles, was studied in detail, the activation energy for each of the deposition modes was calculated.

![Graph](attachment:image.png)

**FIG 2.** - Change of the rate constant of the p-NP reduction reaction for 6 consecutive test cycles (a) and activation energy values for tested samples (b)

THE DECOMPOSITION OF HYDROGEN PEROXIDE

We also studied the possibility of using composite materials based on PET TeM and NTs based on silver as catalysts for the reaction of hydrogen peroxide decomposition [23]. The main objectives of the study were to study the effect of chemical deposition duration of silver NTs from properties of composites with different pore density and the selection of optimal synthesis conditions and to study the effect of temperature from the reaction rate.
The deposition of silver was carried out by chemical template synthesis at a temperature of 4°C, the deposition time was varied from 30 to 300 min, and the test of catalytic activity was carried out in the temperature range 25-45°C.

TABLE 3 - THE DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF CATALYSTS BASED ON SILVER NT AND PET TM

<table>
<thead>
<tr>
<th>Pore density, ion/cm²</th>
<th>Structural parameters of silver NTs, nm</th>
<th>t, min</th>
<th>V (O₂), ml</th>
<th>k, min⁻¹</th>
<th>Ea, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wall thickness</td>
<td>internal diameter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (without irradiation)</td>
<td>-</td>
<td>-</td>
<td>300±10.9*</td>
<td>55.2±4.3*</td>
<td>5.2± 1.2*</td>
</tr>
<tr>
<td>1·10⁹</td>
<td>70.4±4.3</td>
<td>165±17.3</td>
<td>57.3±4.1</td>
<td>15.2 ± 3.4</td>
<td>34.35</td>
</tr>
<tr>
<td>4·10⁷</td>
<td>24.3±1.5</td>
<td>408.4±12.4</td>
<td>180±8.7</td>
<td>59±0.9</td>
<td>13.0 ± 3.0</td>
</tr>
</tbody>
</table>

Note: data are presented with standard deviation for three measurements.

Based on the data obtained, the optimal deposition conditions of silver were determined, corresponding to the highest catalytic activity of composites [23].

ONE-SPOT-THREE COMPONENT MANNICH REACTION

The development of methods for the synthesis of complex nitrogen-containing molecules is of great importance, since the overwhelming number of natural compounds, including proteins, nucleic acids and most biologically active compounds, contain nitrogen. One type of reaction that is widely used in the synthesis of complex organic molecules, such as amino alcohols, peptides, lactams, and others, is the Mannich reaction [34].

We have studied the possibility of using composites based on track membranes and nanostructures of metals of the copper subgroup using the example of the aminomethylation reaction of
acetophenone in methanol [35]. The data on types and dimensions of composite catalysts and conditions for their synthesis are presented in Table 4. PET TeMs with a pores density of $4 \times 10^7$ ion/cm$^2$ and a pore diameter of 410±10.8 nm was used as a matrix. Electron micrographs of synthesized composites are presented in Figure 4.

![Electron micrographs of composites surface](FIG.3)

**TABLE 4 - DATA ON THE NATURE AND COMPOSITION OF TESTED COMPOSITE CATALYSTS BASED ON PET TEM AND METALS OF THE COPPER SUBGROUP**

<table>
<thead>
<tr>
<th>Composite</th>
<th>Dimension of nanostructures</th>
<th>Conditions of composite synthesis</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Internal diameter, nm</td>
<td>NTs wall thickness, nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Height, µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>340.4±11.0</td>
<td>35.8±9.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>Chemical deposition, 48 h</td>
<td>[28]</td>
</tr>
<tr>
<td>Au/Ag</td>
<td>254.0±12.0</td>
<td>77.8±6.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>Chemical deposition, 24 h</td>
<td>[22]</td>
</tr>
<tr>
<td>Cu NPs-PAA-g-PET</td>
<td>Diameter of copper NP, 36.3±9.0 nm</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Chemical deposition of copper with NaBH$_4$ in modified PAA-PET TeM, 1 h</td>
<td>[36]</td>
</tr>
</tbody>
</table>

The catalytic properties were studied for 5 consecutive cycles for all studied composite samples. The optimal reaction time is 24 hours and was selected based on the data of the synthesis reaction yields in the presence of a Cu-PAA-PET-TM catalyst, depending on the reaction time (Fig 4b).
FIG. 4 - Variations in the yield of β-amino ketone with Cu NPs-PAA-g-PET membrane catalysts as a function of reaction time (a) and the yield conversion for 5 tested cycles (reaction time 24 h) for all studied samples

Among the series of investigated samples of composites based on PET TM and nanostructures of metals of the copper subgroup in the aminomethylation reaction of acetophenone, composites with copper NP (78.1%) are most effective in the first test cycle, after the 3rd test cycle, the product yield decreases by 55.1% compared to the first test cycle. However, despite such a high percentage of the yield of the reaction product after the first cycle with the use of gold-based composites and a mixed Au/Ag composition (45.8 and 62.8%) after the fifth cycle, the activity of the catalysts decreased by only 37.7 and 43.8%, respectively, while the catalysts Cu-PAA-PET-TeM almost completely lost their activity.

4 FUTURE PLAN OF RESEARCH

According to our previous research, discussed in previous section, membrane composites with embedded gold, silver and copper nanotubes possess a very high catalytic ability and we are suggesting evaluating these composites for dyes degradation efficiency also.

The main idea of the proposed method of obtaining photocatalytically active ion-track membranes composites is to synthesize metallic nanostructures of various morphologies (nanoparticles and nanotubes) in channels of PET TeMs and also to apply final PET/Metal composites for UV-assisted degradation of different dyes such as methyl violet, neutral red, toluidine blue et al. These
Dyes were selected due to a wide range of applications in different industries and in the staining of bacteriological and histopathological work.

Ion-track membrane with the defined parameters will be prepared on the heavy ions accelerator DC-60 in Astana Branch of INP. Proposed TeMs composites will have a developed specific surface area (pore density of initial TeMs will be varied in the range of $4 \times 10^7$-$1 \times 10^9$ cm$^{-2}$, exhibit high strength and can be easily removed from the reaction mixture after reaction. Various types of nanosized photocatalysts (supported nanoparticles, nanotubes and nanowires et al) were examined and possess a great efficiency in dyes degradation, but for ion-track membranes with embedded metallic nanostructures nowhere else such studies have been conducted.

We are suggesting plating a single/multicomponent component nanotubes as well as metal oxide nanotubes. Among different metallic candidates for electroless deposition in the channels of PET template, copper sub-group metals are a very promising material. Special attention will be passed to the copper: Cu-based nanocatalysts have significant applicability in nanotechnology. In comparison with other noble metals (gold, platinum and silver) recognized as very efficient catalysts, copper is an inexpensive material, 100 times and 6000 times cheaper than silver and gold, respectively [37].

**Working plan for year 1**

- Electroless synthesis and characterization of composite materials based on TeMs and single (Cu, Ag, Au) and multimetallic nanotubes. Improving of deposition procedure.
- Elucidation of the composite membranes structure with SEM, XRD, EDX, TEM techniques.
- Study of the dye’s photocatalytic degradation: Evaluation of dyes (such as methyl violet, neutral red, toluidine blue et al) degradation efficiency, kinetics parameters of studied reactions as well as reusability of catalysts.
- Impact of different parameters (pore density, nanotubes inner diameter, deposition conditions) on the catalytic ability of composite catalysts.

**Working plan for year 2**

- Deposition of metal oxides in pores of PET/polycarbonate templates.
- Determination of optimal conditions using Taguchi robust experiment design.
– Elucidation of the composite membranes structure with SEM, XRD, EDX, TEM et al. techniques.
– Study of the dye’s photocatalytic degradation, evaluation of reusability of catalysts.
– Effect of ionizing radiation treatment on the photocatalytic ability of composite membranes

Working plan for year 3
– Radiation induced synthesis of metallic/metal oxide nanoclusters in channels of PET/polycarbonate templates.
– Elucidation of the composite membranes structure with SEM, XRD, EDX, TEM et al.
– Study of the dye’s photocatalytic degradation, evaluation of reusability of catalysts.

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KOREA

NANOMATERIAL FABRICATION USING RADIATION TECHNOLOGY AND ITS APPLICATIONS FOR ELECTRONIC DEVICES (REPUBLIC OF KOREA)

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Radiation technology has become a core technology in the analysis and synthesis of nanomaterials in Korea. The development of nanomaterials in Korea is subdivided into three research themes, such as advanced IoT (Internet of Things), eco-friendly and healthy people. Advanced Radiation Technology Institute (ARTI) as a branch of Korea Atomic Energy Research Institute (KAERI) is conducting the researches on nanomaterials in various fields such as electronic materials and biomaterials using electron beam accelerators and gamma irradiation facilities. Our team is conducting the researches related to the electronic devices such as solar cell, batteries, electromagnetic (EM) wave shielding, and thermoelectric materials. We introduce EM wave shielding materials for the first year, thermoelectric materials for the second year, and spintronics materials for the third year. Among these research themes, this report will briefly introduce the development of EM shielding materials.

As the performance of electronic device improves, the frequency used in it is also increasing. The radio frequency used in our lives is between 1 and 2 GHz and is expected to increase further. There is a need for an appropriate shielding material due to problems such as interaction of electromagnetic waves between the equipment and influence on the human body. Studies using nano materials are going to increase the resonance frequency of the shielding materials. We will study the application of uniform and high purity nanomaterials synthesized by radiation technology to electromagnetic shielding materials. This material group will start with an iron oxide system and its resonance characteristics at high frequency will be discussed.

NANOMATERIAL FABRICATION USING RADIATION TECHNOLOGY AND ITS APPLICATIONS FOR ELECTRONIC DEVICES
- DEVELOPMENT OF NANOMATERIALS FOR ELECTROMAGNETIC SHIELDING APPLICATION USING RADIATION -

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Abstract

Nanotechnology in Korea is undergoing various studies to improve the wireless network system. The electromagnetic wave shielding material technology also requires improvement of performance in high frequency band. Radiation technology can be used to manufacture nanomaterials that shield electromagnetic wave by inducing magnetic loss. This report briefly describes the synthesis of magnetic nanomaterials using radiation technology and its performance evaluation.

1. INTRODUCTION

Nanotechnology is being integrated with information technology, bio technology and environmental technology to realize innovative materials, parts and system. Nanotechnology in Korea continues to evolve into applied technology fields such as devices, energy, and biotechnology, as well as basic technologies such as materials, processes, and analytical equipment. In recent, interest in artificial intelligence, big data, and high speed communication has increased, and various researches related to nanomaterials have been attracting attention for solving technical difficulties.

Nanomaterials using radiation technology are very fast and simple compared to chemical synthesis methods and physical processing methods and have advantages of being applicable to various materials. However, there is a problem that the speed of development is slow due to a vague risk recognition of radiation. It will be possible to raise awareness if fabrication of nanomaterials using radiation have physical superiority compared to conventional materials, or if economics such as cost reduction are secured. This will be the direction of radiation technology to go forth to enhance the beneficial effect in the nanomaterial researches.

We introduce EM wave shielding materials for the first year, thermoelectric materials for the second year, and spintronics materials for the third year. Among these research themes, this report will briefly introduce the development of EM shielding materials. The use of EM waves plays an important role in the field of communication, studies are underway to establish the wireless communication networks between the objects. As the frequency band gradually increases for faster communication and processing of big data, there is a problem of causing unexpected interaction between electronic devices, and there are many concerns about the effect of EM waves on human body. Therefore, research on developing an EM wave absorber is also being studied using a light material with a thinner thickness in a high frequency. The EM wave shielding mechanism is
generally based on conduction loss, magnetic loss, and dielectric loss. Conductive loss using metal or carbon materials with many free electrons are effective for a relatively wide frequency range, but shielding performance is not high. The dielectric loss is effective in the very high THz band and does not match the normal communication frequency band. The magnetic material is suitable for the MHz to GHz band and has excellent shielding performance and is applied to many wireless communication fields, but the shielding band is narrow. The magnetic loss is caused by magnetic resonance with frequency, and this resonance characteristic can be understood by the Kittel’s equation. This is related to the spintronics material proposed in the third year, so we introduce a special solution to the thin film sample for magnetic resonance as follows [1].

\[
f_r = \frac{\mu_0 \gamma}{2\pi} \sqrt{(H_{app} + H_k)(H_{app} + H_k + M_s)}
\]

where the \(M_s\) is magnetization, the \(H_k\) is anisotropy field, \(H_{app}\) is applied field and, \(\gamma\) is gyromagnetic ratio \((\frac{\gamma}{2\pi} = 2.8 \text{ MHz/Oe})\). In order to improve the resonance frequency, it is preferable to use a material having a high saturation magnetic flux and a large anisotropy field. In addition, the coercivity and resistivity of the material are important factors. The ferrimagnet is a potential material that can meet all of these requirements and the size and shape control are needed to improve the frequency characteristics.

2. EXPERIMENTAL

2-1. Fabrication of iron oxide nanoparticles using electron beam irradiation

The precursor was fabricated by dissolving the FeCl in DI water and adding the NaOH and scavengers such as alcohols. Nanomaterials were fabricated by radiation irradiation such as 10 MeV electron beam on these precursors. The polymeric materials such as PVA are useful to prevent the aggregation. The chemical structure depends on the composition of precursors. The fabrication mechanism is known as follows [2].

\[
\begin{align*}
\text{H}_2\text{O} & \xrightarrow{\text{radiation}} \text{e}_{aq}^-\text{, H}_3\text{O}^+\text{, H}^*\text{, H}_2\text{, OH}^*\text{, H}_2\text{O}_2 \\
\text{M}^+ + \text{e}_{aq}^- & \rightarrow \text{M}^0 \text{ and M}^+ + \text{H}^* \rightarrow \text{M}^0 + \text{H}^+ \\
\text{M}^0 + \text{M}^0 & \rightarrow \text{M}_2 \text{ and M}^0 + \text{M}^+ \rightarrow \text{M}_2^+ 
\end{align*}
\]
\[ M_2^+ + M_2^+ \rightarrow M_4^{2+}, \quad M_m^+ + M^+ \rightarrow M_{m+1}^+, \quad \text{and} \quad M_{m+x}^{x+} + M_{p+y}^{y+} \rightarrow M_{n+z}^{z+} \]

2-2. Characteristics of nanoparticles

Crystal structure of nanoparticles were analyzed using a XRD. The size of nanoparticles was measured by FE-SEM. The magnetic properties such as saturation magnetization and coercivity were evaluated using vibrating sample magnetometer (VSM). The S-parameters was measured using a network analyzer with 7mm air line accessory which was calibrated open, short, load (50 Ω). The complex permittivity and permeability were calculated using a Nicolson and Ross model [3]. Return loss (\(S_{11}\)) were measured using a calibrated 7 mm air line with short.

3. RESULTS and DISCUSSION

Fig. 1. Images of the powders as a function of the irradiation dose.

When the prepared precursor is irradiated with an electron beam, a precipitate is generated as shown in Fig 1. As the irradiation dose increases, the color of the precipitate changes to black. SEM images show spherical particles with a size of about 200 nm irrespective of the irradiation dose. If there is no scavenger in the precursor, no particles are produced at all, but a large amount of addition dose not greatly affect the formation of the particles.

Fig. 2. XRD patterns and magnetic properties of the powders.
From the XRD results, it can be seen that the peak size increases as the irradiation dose increases, and the crystal phase is Fe$_3$O$_4$. It is not shown in this report, when the concentration of Na is high, a powder having Fe$_2$O$_3$ phase is produced. Considering that the particle size in the SEM images is independent of irradiation dose, it is considered that the particles generated at less than 50 kGy were fabricated amorphous phase of FeOH group. As the irradiation dose increases, it is supposed that H$^+$ is replaced to H2 form and removed in gas and the size of Fe$_3$O$_4$ phase gradually increases. These properties can also be confirmed by the magnetic properties of the powder. The saturation magnetization increases up to 300 kGy and then saturated, and the coercivity continues to increase. Considering the physical properties of micro-sized Fe$_3$O$_4$ powder [4], the increase of Fe$_3$O$_4$ phase in XRD was considered to be a direct cause. From the viewpoint of magnetic permeability, it is preferable to have a smaller coercivity than that of a high saturation magnetic flux density, so it can be judged that 200 kGy is suitable.

![Fig. 3. Relative complex permittivity and permeability](image)

The prepared powders were made of a composite material with paraffin wax as a matrix and its relative complex permittivity and permeability were measured. The composite material exhibits resonance characteristics in the vicinity of 2 GHz, and resonance occurs over a wide frequency band, so that the damping constant is considered to be very large.

The relationship between the return loss and permeability and permittivity of the material is given by

$$R.L. = 20 \log \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right)$$
\[ Z_{in} = Z_0 \frac{\mu_r}{\varepsilon_r} \tanh\left( \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right) \]

where \( f \) is frequency, \( d \) is thickness, \( c \) is velocity of light, \( \mu_r \) is relative complex permeability and \( \varepsilon_r \) is relative complex permittivity [5]. Since the complex permeability and permittivity according to the frequency are measured previously, return loss is a function of frequency and thickness as shown in Fig. 4. The return loss periodically peaks according to the frequency and the thickness. Also, a composite material having a high powder concentration causes a higher return loss at a thin thickness.

Fig. 4. Simulated return loss map with different powder concentration.

Fig. 5. Measured and simulated return loss.

In order to see how the calculated results correspond to the actual return loss, specimens with specific thickness were fabricated and measured. These results are shown in Fig. 5. Since the two results are nearly identical, we believe that accurate measurement of complex permeability and permittivity is important.
4. Conclusion

We have conducted research to manufacture iron oxide nanomaterials using electron beam irradiation and investigated the possibility of applying it as an electromagnetic shielding material. By using the developed materials, higher concentration of composite materials can be used as a material exhibiting excellent EM shielding characteristics at a thinner thickness. We are working on the production of nickel ferrite [7] and magnetic nanocomposites combined with carbon materials.

5. Future works

The importance of renewable energy such as solar cells and wind power is increasing with the depletion of fossil fuels. Recently, a thermoelectric element capable of directly producing electricity from a heat source has been attracting attention among the renewable energy devices. The thermoelectric device consists of sequential connections of p-type and n-type semiconductors based on the Seebeck effect. The thermoelectric device is easy to use and lightweight, so it has applicability for portable and wearable electronic devices. In order to improve the performance of thermoelectric devices, it is important to synthesize uniform and high purity nanoparticles. It is known that the nanomaterial can improve the figure of merit by maintaining the Seebeck coefficient and electrical conductivity and decreasing the thermal conductivity. Therefore, thermoelectric materials based on radiation can be expected to have better performance than existing materials.

As information devices using semiconductors reach technological limitations that can no longer reduce their linewidth, technologies that can replace them are needed. Spintronics based information transfer devices are new technologies that use electron charge and spin characteristics together. This device is expected to have low power consumption and greatly improve the operating frequency. The device consists of nanoscale thin films. Radiation (ion implantation technology) can be a challenging technique to control the physical properties of such thin film materials.

6. Acknowledgement
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DEVELOPMENT OF CORE TECHNOLOGY OF SWIFT HEAVY ION BEAM FOR TRACK-ETCHED MEMBRANE

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1. INTRODUCTION

Radiation processing has been developed in basic and applied researches in material science. Among several radiation processes, ion beam technologies have shown its tailoring ability in nanomaterials and nano-scaled engineering. Using particle accelerators, Swift Heavy Ion (SHI) beam can be produced. SHI irradiation on polymer materials gives precise control of changing physical properties of materials such as defect annealing, defect creation and ion track formation. This makes a SHI beam as an excellent tool for creating nanostructures on the polymer materials [1,2]. Using SHI irradiation on a polymer material, latent ion tracks can be formed. This polymer is treated with chemical etching and UV radiation to form several nm ~ um pores through the polymer membrane. It is called a Track-Etched Membrane (TEM). This Track-Etched Membrane production technique can be useful in producing nano-structures on/in polymer samples.

Our main scientific goal is to develop core technologies of SHI beam production suitable for track-etched membranes. Track-etched membrane filters can be applied in water filtration and air (particular matter) filter which are both important in day-to-day life as well as in a disaster. The track-etched membranes can also be used in bio sensors, cell cultivation, electronics and nanostructure processing.

In this project, we plan to build a irradiation facility of Radio-Frequency Quadrupole (RFQ) based 1 MeV/n SHI beam accelerator which will be the sole compact RF heavy ion accelerator in South Korea. In this project, we will employ this facility to fabricate and characterize track-etched
membranes depending upon irradiation control parameters. We expect to secure core manufacturing technologies for track-etched membrane using SHI beams. The entire project is mainly divided into three parts, i.e., SHI beam production, characterization of SHI beam and samples, and SHI beam irradiation system with post treatment processing and evaluation of the membrane.

Through the CRP collaboration, we would share our knowledge of SHI beam irradiation and development know-how of a compact SHI beam facility. SHI beam irradiation can be provided to researchers who share similar interests. We wish to get methods of how SHI beams can be suitably applied to nanoscience and nanotechnology from other state members.

Specific objectives of the project are given below,

1. Development of the SHI beam production technology
   - Extraction of highly charged ions and characterization of accelerating cavities.
   - Design and construction of beam transport and diagnostics system.

2. Characterization of SHI beam irradiation, and construction and testing of sample irradiation system.
   - Simulation studies on interaction between SHI beam and sample such as polymers using the SRIM code.
   - Design and construction of an irradiation chamber.
   - Irradiation on polymers and preliminary analysis of characterization test.

3. Swift heavy ion beam irradiation on polymers and evaluation of the irradiated membrane.
   - Design and construction of the beam irradiation evaluation system.
   - Construction and integration testing of beam irradiation control system.
   - Characterization of SHI beam irradiation on polymer samples.
   - Research on post irradiation-treatment process.
In this report, we present the current status and plans of the project, “Development of core technologies of Swift Heavy Ion beams for Track-Etched Membrane”.

2. MATERIALS AND METHODS

At KOMAC, we have been working on a 100 MeV proton linac and 6 beamlines, various ion sources, implanters and Tandem accelerators, and have operation experiences of large beam facilities. With these bases, we have been developing a Radio-Frequency Quadrupole (RFQ) based ion beam accelerator of the beam energy 1 MeV/n at KOMAC [3]. It will generate SHI beams which are expected to be applied in the research fields of nanoscience and nanotechnology related to the formation of polymer membranes. The RFQ based ion beam accelerator facility consists of an electron beam ion source (EBIS), a set of low energy beam transport (LEBT), a RFQ accelerating cavity, a beam transport system and an irradiation chamber as shown in Fig. 1 a) which is a planned layout of the RFQ based accelerator facility.

The electron beam ion source (EBIS) is one of widely used table-top devices for the production of highly charged ions with a high efficiency of charged state selection. It consists of an electron gun, a magnet, drift tubes and an electron collector. We have two EBIS’s under operation (permanent EBIS and superconducting EBIS) and a 7 Tesla EBIS under development [4]. 7 T EBIS will have higher ionization rate due to high (7 T) magnetic field and larger trap capacity due to 1500 mm
trap length as the trap length of an EBIS is linearly proportional to the trap capacity. The longer trap is the larger trap capacity, leading to larger beam current. Expected ion beam species are Ar, Ne, Kr and Xe highly charged ions. 7 T EBIS is under manufacturing process. Its design layout is shown in Fig. 1 a). Fig. 1 b) is a 7 T superconducting magnet which was manufactured in 2018 and is currently under testing.

![7 T Electron Beam Ion Source design and 7 T superconducting magnet](image)

Fig. 2. a) 7 T Electron Beam Ion Source design and b) 7 T superconducting magnet

7 T EBIS will be first installed with the RFQ accelerator in coming years for larger ion beam current. From the permanent EBIS, we have already extracted Ar ions till the charged state 16, i.e. Ar$^{16+}$. From the EBIS, Kr and Xe ion beams can also be produced. These ions will be injected to the RFQ via the LEBT and get accelerated to 1 MeV/n, producing SHI beams for various scientific researches. Fig. 1. b) shows that the current status of the facility. The RFQ is under manufacturing process as shown in Fig. 3.
Previously at KOMAC, there were proton irradiation studies on polyethylene (PET) to observe effects of 20 MeV proton beams. Pores were formed on the surface of the PET. After chemical etching and UV treatment, we could observe that the pore size got larger. However, the pore channels were not completely through the polymer. This result was obvious for us that lighter heavy ions do not form track-etching even if they have higher beam energy [5]. We think that we can compare various ion species having 1 MeV/n beam energy from our system, studying how threshold energy is affecting the formation of latent ion tracks as a test/investigation to show our RFQ based accelerator and its irradiation system are suitable for membrane studies.

3. RESULTS AND DISCUSSION

The proposed research project is to secure the irradiation technology on poly membranes for the fabrication of Track-etched membrane based on Swift Heavy Ion beam irradiation. At KOMAC, based on our research experience from the development and operations of 100 MeV proton accelerator and various ion beam devices, we plan to build a RFQ based 1 MeV/n SHI beam irradiation facility. Using this facility, our primary goal is to develop the irradiation technology for the fabrication of Track-etched membrane which can be applied to filter manufacturing technologies which is of increasing importance due to environmental reasons. We divide the project into three main objectives, SHI beam production, characterization of SHI beam and samples, and lastly SHI beam irradiation system to fabricate track-etched membranes. Track-etched membrane technology will open up great opportunities not only in filter fabrication but also
in biosensors, cell cultivation, micro/nano structure engineering technologies and electronic devices.Securing core manufacturing technologies for track-etched membrane will contribute to solve environmental problems in the society. This can be applied to safety equipment in hazardous disaster situations. Expansion of utilization of ion beam irradiation on material science will create new industries.

Directly from scientific point of view, the RFQ based 1 MeV/n ion beam irradiation facility will be the sole compact RF heavy ion accelerator to operate in South Korea. This facility will provide ion beam irradiation services to research fields such as semiconductor doping, neutron source development, material engineering (nanomaterials and high temperature superconducting materials), medical radiation treatments etc.

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MALAYSIA

RADIATION PROCESSING OF ELECTROCATALYTS FOR THE ENHANCEMENT OF CATALYTIC PERFORMANCE IN RENEWABLE ENERGY DEVICES

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Abstract
Electrocatalyst plays an important role in enhancing the efficiencies of electrochemical energy conversion devices, such as, fuel cells, metal-air batteries and electrolyzers. The oxygen reactions (oxygen reduction and oxygen evolution) in these devices are kinetically sluggish and relying on high-loading of scarce and expensive precious metals such as Pt as electrocatalyst. Metal oxides have demonstrated promising properties as alternatives to Pt as they are electrochemically stable, have high resistant to corrosion and involve low cost in production. In the form of nanomaterials, the catalytic activities of metal oxides will also be significantly improved due to the large exposed surface areas available as active sites for catalytic reactions. The present study aims to develop a nano-electrocatalyst system based on graphene supported non-precious metal oxides, with performance comparable to the precious metal electrocatalysts system. This will be achieved via microstructural modification and defect engineering using radiation techniques. By irradiating these materials with appropriate dosages of radiations, microstructural change and defect sites favourable to catalytic reactions could be created. Physico-chemical and electrochemical characterizations will also be carried out to study the structure-property relationships of the electrocatalyst system.

1. INTRODUCTION
The increase in global energy consumption has led to an increase in greenhouse gaseous emissions, a critical environmental concern addressed in the United Nations Climate Change Conference. In response to this, renewable energy technology has been given a significant emphasis in Malaysia’s energy policy to meet the country energy demand [1]. Hydrogen fuel cells, metal-air batteries and electrolyzers for water splitting are some of the emerging alternative energy sources with the advantage of low or zero CO₂ emission. These potential energy sources have wide ranging applications in many areas from automobile and aerospace industries to personal devices and gadgets. Studies have shown that it remains a challenge to introduce alternative fuel technologies
in the developing countries, especially in the transportation sector that is still predominantly powered by fossil fuels due to high cost in implementation [2]. In order to increase energy conversion efficiencies of these alternative energy sources, expensive and scarce precious metals (usually Pt-based) are used as catalysts at the anodes and cathodes for hydrogen and oxygen reactions during the device operations. In a hydrogen fuel cell for example, the metal loading at the cathode is even much higher (~10 times higher) than at the anode, due to the complex and sluggish kinetics of oxygen reduction reaction (ORR) [3]. This significantly increases the production cost and is the main hindrance for the commercialization of hydrogen fuel cells.

Research efforts are now focusing on the development of non-precious metals to replace Pt as the electrocatalysts with suitable catalyst supports to increase the total electrochemical active surface areas and to reduce the metal loading at the cathode. Non-precious metal-based materials such as metal oxides and phosphides are promising candidates as electrocatalysts due to the favorable properties they possess in corrosion resistance, chemically stability, electrical conductivity and mechanical strength [4]. Graphene, carbon nanotubes and other porous carbon-based materials are often used as catalyst supports to improve the electrical conductivity and dispersion of the electrocatalysts. A good catalyst support will also provide synergistic effect to the catalyst in enhancing the electrochemical performance [5].

Despite the extensive work reported on enhanced catalytic performance, there is until now, no consensus on the structural features and surface chemistry that are responsible for the observed catalytic reactions in an applied environment. In this respect, the present work aims to study the radiation-induced microstructural and chemical changes on the electrocatalyst system and to establish the structure-property relationships for optimization of the catalytic performance.

2. RESEARCH CHALLENGES

For commercialisation, an electrocatalyst system should be cost-effective, reproducible and can be easily scaled up for mass production. An electrocatalyst may, sometimes, electrochemically stable but structurally unstable. In certain cases of active hydrogen evolution, an electrocatalyst may evolve hydrogen at the expense of corrosion, through the dissolutions of metals into the acidic electrolytes [6]. In view of this, it is important to have an in-depth study on the structural and
chemical evolutions during catalytic reactions. This is to understand the mechanisms of electrochemical and structural stabilities and to determine the active and corrosion sites of the electrocatalyst system. Nonprecious electrocatalysts usually have poorer performance in an acidic medium compared to an alkaline medium. It is, therefore, highly desirable to have an electrocatalyst system that performs well in both media. It is even more desirable to have a bifunctional catalyst that works for both the oxygen reduction and oxygen evolution reactions. Besides functioning well in a fuel cell, in reverse, it produces H₂ and O₂ in a water electrolyzer to feed the fuel cell.

3. ENHANCEMENT OF CATALYTIC PERFORMANCE BY RADIATION

Radiation techniques are often used in defect engineering of materials, leading to changes in their properties. Defects created through irradiation processes may be advantageous to the enhancement of electrochemical properties as they may increase the electron transfer rate. By controlling the coulombic interactions between charged ions and careful selection of the ionic species and irradiation dosages, the induced defects in a catalytic material system could be effectively tailored to meet the desired properties for a particular performance. Some works on the enhancement of photocatalytic effect using heavy ion irradiation have been reported elsewhere [7-8]. Nevertheless, studies on the effects of ion irradiation on the catalytic behaviors of metal oxide catalytic systems for oxygen reactions are still rare. In this work, information obtained from physico chemical characterisations of the catalyst systems, before and after oxygen reactions, will be able to shed some light on the electronic and chemical states of the catalysts during electrochemical polarizations/catalytic reactions, the surface adsorbates, and the active sites for effective catalytic reactions. Besides this, the information on the effects of catalyst loading on catalytic performance and electrochemical active surface areas of the catalysts will be obtained by electrochemical characterization. This will greatly assist the performance optimization of the electrocatalysts via structural and chemical tuning by radiation to suppress the corrosion sites and to increase the exposures of the active sites for optimal catalytic performance.

Various accelerator facilities are currently available in Malaysian Nuclear Agency for performing irradiation on the catalytic materials using electron and ion beams, as shown in Table 1.
TABLE 1: ACCELERATOR FACILITIES AVAILABLE IN MALAYSIAN NUCLEAR AGENCY

<table>
<thead>
<tr>
<th>Types</th>
<th>Source</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nissin EBM (“Electron Beam Machine”) Japan</td>
<td>Electron</td>
<td>3 MeV, 30 mA</td>
</tr>
<tr>
<td>ELV4-Russia</td>
<td>Electron</td>
<td>1 MeV, 50 mA</td>
</tr>
<tr>
<td>Curetron-Japan</td>
<td>Electron</td>
<td>200 keV, 10 mA</td>
</tr>
<tr>
<td>Plasma focus</td>
<td>Argon ions</td>
<td>3.375 kJ, 13.5 kV</td>
</tr>
</tbody>
</table>

4. RESEARCH OBJECTIVES

The present electrocatalysts used in renewable energy devices are faced with two major problems, namely, the kinetically sluggish oxygen reactions and the high production cost. Besides this, information on the catalytic effects arisen from defect engineering and microstructural modification via radiation is scarce. In this work, we shall investigate the effects of radiation on the catalytic performance of nano-electrocatalyst system based on non-precious metal oxides and their graphene supports with the following objectives:

- To analyze the defects and microstructural changes resulting from the effect of radiation on the nano-electrocatalyst system
- To identify the suitable radiation conditions (radiation species and dosage) for the nano-electrocatalyst system for optimized electrocatalytic performance.
- To study the structure-property relationships and the catalytic mechanisms of the irradiated nano-electrocatalyst system

5. RESEARCH METHODOLOGY

(a) Synthesis of graphene
A 3-electrode potentiostat will be used with pure graphite as the working electrode, Pt plate as the counter electrode and Ag/AgCl as the reference electrode in 0.5 M sulphate-based electrolytes such as H₂SO₄. The graphite is immersed in the electrolyte and exfoliation is conducted by applying a DC voltage (1 – 5 V) to the anode for a short duration (10 s – 2 min), followed by a higher DC voltage (10 – 20 V) for a duration long enough to exfoliate sufficient amount of graphene oxides. The exfoliated graphene oxides flakes are washed, filtered, centrifuged and dried in vacuum oven. The oxygen content in the graphene oxides flakes are reduced electrochemically via linear sweep voltammetry (LSV) or by high temperature treatment to yield reduced graphene oxides with structures close to pristine graphene.

(b) Synthesis of Metal Oxides

Oxides from the transition metals (cobalt oxides, iron oxides and nickel oxides) will be synthesized by precipitation from their precursors. By adding the precursors drop wise into 1 M NaOH under sonication, the precipitates formed are subsequently centrifuged and dried overnight at 100°C in an oven. This is followed by calcination in air inside a box furnace at 300°C for 3 hours. In this way, metal oxides of nanosized dimensions will be obtained.

(c) Structural modification by ion irradiation

Structural modifications of the metal oxides and its graphene supports will be carried out by irradiating the catalyst systems with electron beams or ions beam from a plasma argon source. The effects of irradiation on the microstructural changes, electron transport and catalytic performance of the materials will be systematically investigated.

(d) Physicochemical Characterization

All electrocatalyst systems on their supports will be characterized using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) Transmission Electron Microscopy (TEM), Energy dispersive X-ray Spectrometry (EDX), Simultaneous Thermal Analysis (STA), Raman Spectrometer and Atomic Force Microscopy (AFM) techniques for details on microstructure, dimensionality, morphology and chemistry. Materials distribution (density) and the orientation of electrocatalysts on their carbon supports will also be studied. X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Near Edge Structures Spectroscopy
(XANES) and High Resolution Transmission Electron Microscopy (HRTEM) will be employed on the electrocatalyst system to provide information on the electronic and chemical states of the electrocatalysts, the surface adsorbates, particle sizes, surface area and the preferable active sites for effective catalytic reactions.

(d) Electrochemical Characterization

Electrochemical characterizations will be carried out to access the performance of oxygen reactions (Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER)) of the electrocatalyst systems. Three-electrode setup of an electrochemical cell with rotating ring disc electrode (RRDE), glassy carbon and reversible hydrogen electrode (RHE) as the working electrode, counter electrode and reference electrode respectively, will be used for all the electrochemical characterizations. In brief, ORR and OER will be carried out in the electrochemical cell both under oxygen saturated (for ORR) or nitrogen saturated (for OER) alkaline (0.1 M KOH) and acidic (0.1 M HClO₄) media. Cyclic Voltammogram (CV) will be obtained from a complete cycle of electrochemical polarizations under ORR (0 to 1 V vs. RHE) and OER (1.2 to 1.8 V vs. RHE) potential windows. The ORR and OER kinetics will be analysed from the current densities and onset potential in CV. The detailed kinetic studies and catalytic reaction pathway will be performed via the analyses of Tafel and Koutecky-Levich Plots. During ORR, the ring potential of RRDE is set to 1.2 V to oxidize the H₂O₂ produced for H₂O₂ detection. Apart from theoretical analysis from Koutecky-Levich Plot, this provides the experimentally insights into the catalytic reaction pathways involved. The RRDE was set to rotate (at different speeds) to increase the rate of mass transport of the reactants to the electrode or the catalyst surface, and to facilitate the study of charge-transfer kinetics under the mass transport limitation during ORR. Corrosion resistance and electrochemical stability of the electrocatalyst will be carried out using the Chronoamperometry tests (at least 8 hours) and a slow scan rate analysis at 0.1 mV/s. Electrochemical Active Surface Area (ECSA) and Electrochemical Impedance Spectroscopy (EIS) will also be performed to access the active surface areas and electrical conductivities of the electrocatalysts respectively.

All the electrochemical characterizations will be repeated for commercially available Pt on in-house synthesized graphene for comparisons. The synthesized non-precious transition metal oxide
catalysts will be benchmarked against the commercial Pt on carbon black (Pt/C). Sample with behavior closest to the commercial Pt/C will be analyzed in-depth for the structure-property relationships and the kinetic processes involved in the catalytic reactions. The flow chart in Fig. 1 summarizes the experimental stages involved.

**FIG.1:** Schematic diagram showing the workflow

6. OUTLOOK

This study aims to exploit radiation technology to produce a durable, high performance and yet cost-effective nano-electrocatalyst system based on graphene supported non-precious metal oxides for renewable energy applications. It is hoped that this will pave the way for the use of inexpensive radiation-modified non-precious materials for enhanced catalytic performance in fuel cell and other related technologies. On the socio-economic aspect, it is envisioned that the research output will open a new arena in the development of nano-electrocatalysts systems based on non-precious materials that would be highly beneficial to the economy of the hydrogen technologies in applications ranging from transportation to portable electronic devices. These developments would
have a positive impact on Malaysia’s social economy development and help in reducing the country’s carbon footprints.

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MOROCCO

EXPLOITATION OF RADIATION INDUCED EFFECTS FOR THIN FILM: PHOTOVOLTAIC AND ELECTRONIC APPLICATIONS.

A brief Introduction on the project team is given as well as the main R&D topics conducted in the involved laboratories.

The project is submitted jointly by partners from material Science Unit in national Centre for Energy, Science and Nuclear techniques in Morocco, and the CEMHTI in Orleans-France.

The team is working on material science with more focused topics on functional materials applied in renewable energy in particular solar PV and hybrid thermo-PV cells. With the same team, we have initiated and participated to a European Commission project “EUROSUNMED” dealing to exploitation of solar energy in the Mediterranean region, from 2013 to end of 2017, and also we are participation in other projects dealing to water desalination using solar energy in remote area, and development of smart system for agriculture; in the R&D we have also designed a thermo-PV solar hybrid modules, which is under procedure for patent.

After this brief introduction of our team, I will do my presentation following this plan:

- Introduction: World energy context
- Photovoltaic context
- Kerf-less processes: State of the art
- Objectives of this work
- Proposed research work plan
- Conclusion

As introduction, the World Energy Context and the problems related to energy will be given namely regarding the need vs. the available resources. More than 85% of the current world energy comes from fossil fuels (crude oil, natural gas and coal) resulting in about 76% of the CO₂ emission.
In addition to the problem of CO$_2$ emission, fossil fuels reserves are decreasing, and estimations predict that they will become unavailable in 53 to 109 years, respectively for crude oil and coal.

For these reasons, most of the countries are working on other energy resources, limiting both the CO$_2$ emission and the energy cost. The most general renewable resources being: solar, wind, hydroelectric, biomass and geothermal.

After this general energy worldview, the Moroccan Energy Strategy will be explained with the recent development in renewable energies and the corresponding plants being installed in Morocco [1].

Morocco imports 97.5% of energy to fulfill its need. Energy is considered as a driver for major projects launched in all sectors: Tanger Med, Emergence, Off-shoring, Azur Plan, Green Morocco Plan, Cement, social housing, new industrial zones…

The energy sector, particularly renewable energy, is among Morocco's national priorities expressed in the national energy strategy and the national priority research programs since 2009 [1]. In order to cover its energy needed with lower costs, Morocco has developed the National Energy Strategy. In this strategy, the objective is to cover 42% of its electricity needed from renewable energies by 2020 (2000 MW from wind, 2000 MW from solar and 2000 MW from hydro), rising to 52% by 2030, with solar, wind and hydropower each providing a third of the total energy. The projects NOOR of Ourzazate in south of Marrakech have been launched and began to produce electricity, other plants like Noor Midelt are under construction.

Among the renewable energy sources, the solar radiation offers a huge potential with both thermal and photovoltaic possibilities. The talk will be more focused on photovoltaic conversion. The solar potential in terms of solar radiation will be given, followed by the power capacity and costs related to PV option. Currently, 1st generation solar cells represent about 92% of the PV market (56% of multi-Si and 36% of mono-Si) based on Silicon of 180 µm thickness. This is up to 65% of the total module cost [2]. Many technologies have been developed based on thin films in the objective of costs reduction and performance increase.

The physics background on PV conversion on semi-conducting material will be recalled and the technical aspects will be discussed. In particular, the standard method for cutting thin films from bulk material, such as sawing, have relatively high energy consumption, and lead to a material loss
of up to 50% weight, and require appropriate surface post-treatment [3]. This has an impact on the cost of solar panels. Therefore, currently, cost reduction is one of the main problems in the photovoltaic area [4]. One of the solutions of cost reduction consists on lowering the quantity of Silicon used in PV cells. Several Kerf-less processes will be introduced as a solution to produce ultra-thin substrates, hence reducing the material loss. The advantages and disadvantages of each process will be analyzed. Then, the process projected in this work will be described.

Faced with the limits to minimize the thickness of substrates by the standard wire saw technique, many teams have developed new approaches that, to date, are at more or less advanced degrees of maturity. The ultimate goal was to produce thin layers of crystalline silicon with thicknesses between 10 μm and 100 μm, while avoiding material losses inherent to the sawing step. Such raw material savings would indeed reduce the consumption of purified silicon by a factor of 2 to 10. Some of these approaches are:

- Porous silicon growth processes, which are based on the epitaxy of an active silicon layer on a porous silicon structure [5-11],
- Stress detachment processes, which are based on the detachment of a silicon thin film by applying a strong stress field on a wafer, so as to propagate a crack at a given depth and parallel to the surface [12-14].

Despite these research and development, these processes showed their limitations such as [15]: surface roughness of exfoliated layers, poor control of the thickness of exfoliated layers and photo current decreases with absorber thickness.

Exfoliation processes by implantation of hydrogen make it possible to overcome these problems. Indeed, the implantation of hydrogen induces defects in the structure to a precise depth, which creates a weakened zone. The material is bonded to the substrate on the thin layer face and the detachment of the rest of the material is done by applying a mechanical or thermal stress. In the literature, there are two different approaches to exfoliation by implantation of hydrogen: one at low implantation energies (a few tens of keV) and another at high implantation energies (a few MeV). The high energy technique and the low energy one is used in the Smart-Cut © process [16]. The latter uses the implantation energy generally between 20 keV and 250 keV, which corresponds to an implantation depth of ions ranging from 0.03 μm to 2 μm. In addition, after the transfer of the thin layer by Smart cut process, a growth step is necessary to thicken the transferred layer and
reach the thicknesses compatible with photovoltaics. All these steps are too expensive to address the solar cell market. For that, in this present work, we use the high energy hydrogen implantation. The feasibility of this detachment method approach was first demonstrated in CEMHTI-Site cyclotron by H. Assaf et E. Ntsoenzok [17]. These authors made self-supporting silicon films (111) with thicknesses ranging from 9 μm to 48 μm, for implantation energies of 650 keV at 2 MeV and fluences of $5 \times 10^{16}$ H/cm² and $8 \times 10^{16}$ H/cm². In addition to these works, Braley et al. on the silicon samples (111) and (100), which retain an important place in the state of the art of the current high-energy implantations [18]. Indeed, the authors have shown that the fluence required for detachment varies according to the orientation of the material used.

Implantation of hydrogen in silicon results in a hydrogen supersaturation at a given depth depending on the ion energy, as well as the formation of extended defects as platelets or nanocavities; the application of a stress then makes it possible to detach the thin layer from the rest of the material. The advantage of this technique is that it allows manufacturing of thin layers of reduced thickness, kipping unchanged the quality of the bulk material that can be re-used for further thin layer cutting [19].

This project aims to carry out a complete fundamental work on the defects induced by implantation in Silicon as well as their evolution with different heat treatments. All these data should allow the realization of reliable models (similar to those made with Silicon by Smart Cut for electronic application) on the formation of defects extended parallel to the surface in silicon. These models will be used to support fault engineering and develop technological applications for photovoltaics and electronics via thin film formation by implantation technique.

In this project, we propose to investigate key factors behind scientific challenges in implantation (ion dose and energy), and thermal treatment (temperature, time) conditions, in order to optimize the experimental conditions for a better quality of the thin film detached by implantation. In particularly, for Silicon, Sapphire and GaN, widely used in solar cells, displays and spintronic components.

The samples prepared in CNESTEN and implanted by hydrogen ion beam using Van de Graaf accelerator of CEMHTI-Site Cyclotron, will be studied by using different complementary characterization techniques, such as photoluminescence (PL), Raman, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Ultra violet (UV) spectrometer, surface roughness
measurement, transmission electron microscopy (TEM) in both research centers CNESTEN and CEMHTI-Site Cyclotron.

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PHILIPPINES

RADIATION-INDUCED SYNTHESIS OF NANOSTRUCTURED MATERIALS FOR ANALYTICAL APPLICATIONS

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Abstract

Since the initial application of the surface plasmon resonance (SPR) for gas detection and biosensing was demonstrated in 1983, SPR sensing has been receiving a lot of attention from the global scientific community. For the development of effective SPR sensors, the immobilization of the recognition functional groups or molecules is always required. Imparting these groups on the SPR gold substrate allows the formation of the covalent, ionic, or hydrogen bonds between analyte molecules and the surface. Generally, an adequately high surface concentration of functional groups as well as immobilized layer stability in the target solution matrix is required. This study will be conducted to determine the possibility of using reversible addition-fragmentation chain transfer (RAFT) – mediated radiation-induced graft polymerization in imparting polymers bearing selected functional groups on the surface of a chemically modified SPR gold substrate. The effects of different parameters that affect the chemical modification of the SPR gold substrate and the radiation-induced graft polymerization of selected monomers from the modified gold surface will be systematically studied. The performance of the radiation-grafted SPR gold substrate in the analytical determination of selected environmental contaminants will be evaluated.

INTRODUCTION

The application of surface plasmon resonance (SPR) for gas detection and biosensing was demonstrated in 1983. Since then, the great potential of SPR sensor technology for the detection of chemical and biological substances has been getting growing interest from the scientific community. Currently, SPR-based technologies are increasingly employed, not only in chemical and gas sensing, but also in many other important applications in food safety, biology, and medical diagnostics. Examples are the detection of E. coli in fresh spinach by SPR spectroscopy, serotyping of Salmonella by SPR, sensing of living cells, detection of ammonia, hydrogen sulfide and nitrogen dioxide, and in combination with anodic stripping voltammetry, SPR method has been utilized for the detection of copper and lead ions [1].

Surface plasmon resonance is a charge-density oscillation that may exist at the interface of two media with dielectric constants of opposite signs, for instance a metal and a dielectric. The charge density wave is associated with an electromagnetic (EM) wave, the wave vectors of which reach their maxima at the interface and decay evanescently into both media. This surface plasma wave or surface plasmon polaritons is a polarized wave that has a magnetic vector perpendicular to the direction of propagation of the surface plasma wave and parallel to the plane of the interface. The propagation of the surface plasma wave is supported by the conditions fulfilled by several metals...
of which gold and silver are the most commonly used [1]. In optical sensors based on surface plasmon resonance, the surface plasmons are excited by light waves. Surface plasmons can be optically excited if the phase-matching condition is fulfilled, i.e. the projection along the x-axis of the incident light wave vector matches the propagation constant of the surface plasmons [2].

The promising potential of SPR sensors lies in the very high sensitivity of surface plasmons excited at a metal-dielectric interface to a change in the refractive index of the dielectric. A change in the refractive index of the dielectric or sensed medium results in a change of the propagation constant of the surface plasmons. This change subsequently alters the resonance condition between the surface plasmons and the interacting optical wave. Based on the measured characteristics of the optical wave interacting with the surface plasmons, SPR sensors can be categorized as sensors with angular, wavelength, intensity, or phase modulation. Of these different modulation schemes, the angular and wavelength modulations are the most commonly employed in SPR sensors owing to their high resolution and relatively simple instrumentation. An SPR-based sensor is made up of an SPR sensor and suitable surface functionalization acting as the recognition or sensing site. When an interaction, such as binding of analytes, the refractive index near the surface is altered. This modification of refractive index can then be detected by the SPR sensor. Therefore, the overall performance of an SPR sensor depends on the intrinsic performance of the SPR sensor and the characteristics of the surface functionalization.

The overall performance of an SPR sensor is affected by the characteristics of the surface functionalization. The most commonly used approach is through covalent attachment of the receptor molecules/functional groups on the metallic film supporting the propagation of charge density waves [2]. The covalent immobilization strategies include chemical reactions such as amino, thiol or aldehyde coupling on previously formed functional self-assembled monolayers on gold surfaces. The use of polymers to modify the gold layer is also an alternative. Most of these polymers are applied as thin films on the gold SPR films. Electrodeposition of thin oligomeric or polymeric films from solution/emulsion monomers is a convenient way to modify the surface of the conducting material in SPR sensors because it allows easy control of the thickness and uniformity of the polymer layers. Surface-initiated polymerization or grafting-from approach is another technique that may be employed to modify the surface of the gold layer in SPR sensor.
The grafting-from approach is based on immobilization or production of initiator on the surface of sensor substrate, which can be accomplished chemically or through the use of ionizing radiation.

Radiation processing is a unique tool for synthesis of nanosized polymers of various types and offers a promising alternative to conventional synthetic methods because (1) it is friendly to the environment because it expends less energy, (2) creates less waste, and (3) utilizes less chemicals. In recent years, an increasing number of papers have been published on ionizing radiation-induced graft polymerization of natural and synthetic polymers [3 – 12] mostly because of the fact that the methods using ionizing radiation are often easier to handle than most conventional chemical techniques. Electron beams and γ-radiation are examples of high-energy radiation that are used by researchers worldwide to initiate polymerization from solid surfaces, which generally proceeds via free radical polymerization process. Polymerization by radical initiators (chemically or through ionizing radiation) from the gold surface poses a challenge because of the irreversible termination of propagating polymer chains and chain transfer reactions. Both irreversible termination of propagating polymers and chain transfer reactions result in a loss of control over chain length (i.e. thickness of polymer film) and chain structure together with broadening of the molecular weight distribution [13 – 15]. These drawbacks have led to the research area of controlled free-radical polymerization (CRP), a group of polymerization techniques that relies on reversible transfer processes, which can be utilized to control the polymer architecture and to reduce polydispersity. Two such types of CRP are the atom transfer radical polymerization (ATRP) and reversible-addition fragmentation chain transfer (RAFT). Both techniques are known to produce high polymer segment densities that cover the underlying substrate and can form relatively uniform polymer surfaces with controllable layer thicknesses at the nanoscale level. However, only the RAFT method has been found to be compatible with ionizing radiation as mode of initiation, thus it is the technique of choice for this study.

The uniformity of the polymer layer and controllability of the thickness must be considered when applying polymers in the modification of the SPR sensor's gold interface. These two factors could be attained by RAFT-mediated grafting. In a research paper by the group of Guven, poly (acrylic acid) (PAA) was grafted into the nanochannel walls of track-etched poly(vinylidene difluoride) (PVDF) membranes in a controlled manner by reversible addition fragmentation chain transfer (RAFT)-mediated radical polymerization [16]. The technique they used in the study allowed the formation of covalently bonded PAA in nanopore surface. Without chain transfer
agents, i.e. RAFT agents, the polymerization was not controlled and the nanopores were inevitably filled-up, resulting in constrained and blocked nanochannels. However, the application of RAFT agents during polymerization imparted chain length control, which was observed from the AFM images and by analyzing the pore diameters of membranes and molecular weight of free polymer obtained. The results demonstrated that chain growth from the nanochannel walls is a controlled process, and that the grafted polymer thickness, which corresponds to the chain length, can be easily manipulated by adjusting the ratio of added RAFT agent to monomer and monomer conversion.

In this study, commercially available SPR gold substrates will be modified by a two-step process: (1) chemical modification by reaction with thiol- or mercapto-compounds to form self-assembled monolayer of an alkyl chain-containing molecule; (2) RAFT-mediated radiation-induced graft polymerization of selected monomers from the surface of chemically modified SPR gold substrates. The free polymers formed during the RAFT-mediated polymerization will be tested by gel permeation chromatography (GPC) to determine molecular weight and molecular weight distribution. The surface properties of the grafted SPR gold substrates will be evaluated using Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), tunneling electron microscopy (TEM) and contact angle analysis. The performance of the sensing film in the analytical determination of herbicides and other environmental contaminants will be evaluated. For the Year 1 of this study, the activities will focus on the modification of the SPR gold substrate by radiation induced grafting.

MATERIAL AND METHOD

MATERIALS

Commercially available SPR gold substrates will be used in this study. It is composed of borosilicate glass with 5-nm chromium layer for adhering the gold layer, and then at most 50 nm gold layer for better plasmon wave generation. Analytical grade monomers, RAFT agent and solvents will be used in the chemical modification and radiation-grafting processes.
SPR GOLD SUBSTRATE MODIFICATION

Figure 1 shows the general scheme for the modification of the SPR gold substrate. Modification of the SPR gold substrate will be carried out by RAFT-mediated radiation-induced graft polymerization of selected monomers from the surface of chemically-modified SPR gold substrate. The effects of the following parameters will be systematically studied: for the chemical modification of the SPR gold substrate (1) thiol- or mercapto- compound concentration, (2) reaction temperature, and (3) reaction time; for the RAFT-mediated radiation grafting (1) monomer concentration, (2) monomer to RAFT ratio, (3) solvent, (4) absorbed dose, (5) presence of surfactant (if applicable).

EVALUATION OF CHEMICALLY MODIFIED AND GRAFTED SUBSTRATE

The surface properties of the grafted SPR gold substrates will be evaluated using FTIR, XPS, SEM, EDX, TEM and contact angle analysis. The free polymers that will be formed during the employment of simultaneous grafting technique will be analyzed by GPC to determine their molecular weight and molecular weight distribution, which could provide estimates about the properties of the grafted polymer chains.
WORK PLAN

Year 1-2:

(1) Characterization of commercially available SPR-gold substrate.

(2) Functionalization of the SPR-gold substrate via thiolation and characterization of the self-assembled monolayers forming therefrom.

(3) Optimization of radiation-induced RAFT-mediated polymerization of selected monomers from the surface of functionalized gold substrate. Factors for optimization include absorbed dose, absorbed dose rate, monomer concentration, monomer-to-RAFT ratio, and solvent.

Year 3:

(1) Optimization of radiation-induced RAFT-mediated polymerization of selected monomers from the surface of functionalized gold substrate. Factors for optimization include absorbed dose, absorbed dose rate, monomer concentration, monomer-to-RAFT ratio, and solvent.

(2) Characterization of the nanostructured polymer grafted from the modified gold substrate. Techniques that would be used include SEM-EDX, FTIR, XPS, GPC, TGA, DSC.

Year 4:

(1) Application of the radiation-modified SPR-based sensor in the analytical determination of pollutant compounds. The surface plasmon resonance (SPR) spectroscopy will be used as the main technique for the quantification of the selected compounds.

TEAM

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REFERENCES

POLAND

RADIATION SYNTHESIS OF POLYMER- AND METAL-BASED NANOMATERIALS
- NEW METHODS AND PRODUCTS

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Introduction

It has been recognized that the most promising application fields of radiation-assisted nanotechnology that will be developing in the nearest future are environmental protection and remediation, electronics and energy, medicine and healthcare, chemical industry, advanced functional materials, food and agriculture. The general aim of this project, being a part of the CRP, is to address some of the specific challenges which have been identified by participants of TMs held in November 2017 and April 2018 from many Member States regarding the most urging topics in the field of radiation-synthesized nanomaterials and to fill the scientific and technological gaps between the current state of the art and the emerging needs in application of radiation technology in nanomaterials and nanoprocessing. These gaps and challenges include control of the key parameters in radiation processing of nanomaterials, control of morphological parameters, methodological aspects and also the technical challenges. The specific problems that we propose to address as CRP participant are described below.

TASK 1.

In recent years significant progress has been made in radiation synthesis of nanogels and advanced studies are under way to elaborate products for medical use based on these materials. Also, techniques for surface modification on the nanoscale by synthesizing thin polymer layers using radiation grafting are well developed. However, most of these techniques and products are based
on the use of synthetic monomers or polymers. While this approach has some advantages (large variety of chemical structures available, relatively easy process control), with the current general shift of paradigms in science and industry, we are inclined to seek for "greener" technologies and products which use biobased resources, e.g. substrates based on natural polymers. Polysaccharides are a natural choice, but the well-known problem of employing them in radiation processing is that nearly all of them predominantly degrade under the action of ionizing radiation, and thus they cannot be efficiently cross-linked. At our labs we have developed several methods that allow for radiation-induced crosslinking of polysaccharides. So far, these methods have been proven to work in the synthesis of macroscopic materials. In this CRP we undertake to elaborate new approaches which would allow for radiation synthesis of nanoparticles and nanolayers based on natural polymers. The products, having biocompatible and biodegradable properties, could serve as nanotechnology platforms for various products, for instance in the fields of environment protection, healthcare and agriculture.

Our activities within this topic will include testing and selecting appropriate natural polymers as substrates, performing moderate modifications to their chemical structure to make them suitable for radiation processing, characterizing the starting and modified materials and checking their reactivity under irradiation, elaborating the nanoprocessing procedures, performing and optimizing the synthesis of at least two kinds of nanomaterials (with many options regarding the final properties), i.e. nanogels/nanoparticles and nanolayers, using these biobased substrates, testing the product properties and elaborating the perspectives of using them as application platforms.

The following tasks are planned for the first year. Processing natural polymers (mainly polysaccharides) into their derivatives which will serve as substrates for nanomaterials synthesis. Characterization of these derivatives and testing their reactivity under irradiation. Performing preliminary tests on the radiation synthesis of nanostructures (including nanogels) based on the above-mentioned derivatives and characterization of the products.

The expected final output of this tasks will be developed methodologies for synthesizing, using radiation technique, various nanomaterials (including nanoparticles and nanolayered surfaces) from biobased substrates, namely natural polymers.

TASK 2.
Rapid progress in nanotechnology is not quite fully matched with development of suitable research- and design tools. This is also true for radiation synthesis of nanomaterials. We will develop new experimental and simulation methods allowing for deeper understanding of the chemical reactions and physical processes underlying radiation-assisted formation of polymer nanomaterials and for better and more efficient planning of such radiation syntheses.

Within this project we propose to develop and test two new tools for studying the aforementioned effects, one experimental and one based on simulations. (a) Most reactions induced in polymer systems by ionizing radiation occur by free radical mechanisms. Due to the short-lived character of many radical species, these processes are often very fast and therefore difficult to follow. While some of them can be studied by classical pulse radiolysis with spectrophotometric detection, the latter is often not specific enough to observe the most important free-radical processes in polymers, i.e. polymerization, inter- and intramolecular crosslinking, degradation, depolymerization and also changes in size, shape, conformation of macromolecules or polymer nanoparticles. Based on our original approach, we propose to develop and test pulse radiolysis setup with multi-angle laser light scattering detection. This technique will allow direct, time-resolved observation of the most important reactions used in the synthesis and modification of polymer-based nanoparticles. Preliminary steps in this direction (general design and a prototype) have been already made; and within this CRP we will further develop the system to make it fully functional. We will also run tests in order to demonstrate its applicability and advantages in studying radiation-assisted nanoparticle synthesis. (b) Moreover, in co-operation with external partners, we will contribute to development of new computer simulation tools able to predict and describe chemical reactions and physical processes in irradiated polymer systems, with special emphasis on understanding the processes occurring at the nanoscale and involved in nanoparticle synthesis and modification.

The radiation-induced polymerization and cross-linking is one of the easiest, most effective and “clean” methods used to synthesize polymer hydrogels. In spite of its popularity, the kinetics of this complex process is still insufficiently known, because of the problems with separation of elemental kinetic factors on the experimental way. Additionally, the richness of competitive reactions and excluded volume phenomenon in this kind of complex systems significantly hinders the experimental studies. In this Project we will study some of the important processes involved in polymer formation and modification, in order to deepen our understanding of the dynamics and mechanism of these reactions. Proposed approach is novel and innovative for at least two reasons.
First of all, parallel experimental work and computer simulations will be performed. Secondly, both the selected simulation and experimental approach are based on original concepts that have been so far rarely used to explain general phenomena in polymer physics and chemistry.

DLL (Dynamic Lattice Liquid) [T. Pakula, J. Mol. Liq. (2000) 86, 109] is based on a lattice structure, i.e., positions of the system basic elements, called grains (molecules, set of molecules or monomer units) are regarded as lattice sites. It is assumed that molecular system has some excess volume, therefore molecules have enough space to vibrate around their position defined by the lattice sites (this is considered as attempted displacements). However, they cannot move easily over the larger distance because all the neighboring lattice sites are occupied. Consequently, most of the attempted displacements finish with return to the initial position. Successful attempts are made only for local grain groups with sum of displacement vectors equal to zero. As a result only paths in the form of closed loops can satisfy this condition. The algorithm defined by DLL model starts with the random selection of unit vectors which are assigned to the grains and represents movement attempts. An example of such assignment of attempted directions of motion is shown in Figure 1 (for simple liquid on triangular lattice). All beads which do not contribute to correlated sequences (loops) are immobilized.

![Figure 1. Schematic representation of molecular system in DLL algorithm. The vector field represents displacement attempts in the direction of the neighboring lattice sites. Example of rejected move: (1) collision, (2) attempt to create a vacant site, (3) attempt not participating in closed loops; accepted move: (4) cooperative loop. Courtesy of Chair of Molecular Physics, Lodz University of Technology.](image)

One can distinguish following basic steps in described algorithm: (i) generation of vector field representing attempts of moves, (ii) finding all successful attempts in the whole system, (iii)
performing the reaction if given grain and randomly selected neighbor contains substrate (e.g. radical) and (iv) moving grains along closed loops to neighboring lattice sites. Steps (i)-(iv) define one simulation step 1 MCS and during simulation run MCSs are repeated many times (always with a new set of randomly chosen vectors). In long time limit Brownian motion is obtained for every grain if there are no motion constrains.

Computer simulations, based on the DLL approach (conducted on local computer cluster at Lodz University of Technology (TUL), supported by ARUZ device (computer dedicated for simulations of parallel processes) and PL-Grid infrastructure) can not only reduce the cost and duration of testing some hypothesis when compared to experiments, but allows to go beyond of what is possible to measure experimentally. Single processes can be easily isolated and tested in precisely controlled conditions with elimination of unwanted side factors and experimental errors, as well as technical limitations. However, as with any new tool, proposed approach must be carefully tested. That is why we first will be verified if simulation approach and model reproduce well these situations that can be studied experimentally (radical formation, polymerization, cross-linking in different concentration regimes etc.).

Several main topics will be analysed:

3. Reactions of small molecules/radicals with macromolecules at various concentration regimes.
5. Intramolecular reactions of single and multiple radical pairs on polymer chains: formation of nano- and microgels.

Developed, new, ready-to-use techniques for studying and predicting chemical reactions and physical effects involved in the radiation synthesis of polymer-based nanomaterials: (a) pulse radiolysis system with multi-angle laser light scattering detection, (b) simulation tools.

TASK C.
Metal nanoparticles constitute one of the major current materials in nanotechnology, with many products already on the market and strong perspectives for further growth. It is also known since some time that metal nanoparticles can be synthesized using ionizing radiation and that this method has some important advantages over the typical chemical ones, the main one being the absence of chemical reducing agents. However, there are also some not yet fully understood factors which may influence the outcome of radiation syntheses, including product properties and stability. This may also cause reproducibility problems and makes it difficult to compare results obtained at different laboratories. It may also discourage research labs and industry from applying the method. At IAEA there is a body of experience indicating that such problems can be tackled by performing well-planned interlaboratory studies. Since among the candidate participants of this CRP there are a number of labs having some experience in radiation synthesis of metal nanoparticles, the accumulated knowledge and experience can be used in preparing a good plan for such a study, identifying the critical factors, establishing ways of dealing with potential problems and finally for running an interlaboratory study on one or more products. Such a study may not only lead to an increase in experience, skills and self-confidence of the participating laboratories, but also, in future, in greater confidence in the reliability and reproducibility of the radiation technique for the synthesis of metal nanoparticles.

If the CRP Partners decide to launch an interlaboratory study, the tasks will be the following. Exchanging experiences and up-to-date results between the participating labs that have been so far involved in radiation synthesis of metal nanoparticles. Discussions leading to identification of the critical factors influencing the reproducibility of the synthesis as well as properties and stability of the products. Establishing, upon discussion with other partners of this CRP, plans and protocols for performing the inter-laboratory exercise on radiation synthesis of metal nanoparticles. Preliminary testing the protocols at 2-3 labs. Sending out the protocol to all interested CRP partners. Performing the syntheses by all involved partners in a controlled and documented way, followed by product analysis (again by using agreed techniques and protocols) and sending the samples to a designated analytical lab for detailed studies and comparisons. Elaborating and disseminating the results, discussion on the outcomes.

The final outcome should be an established, proven protocol for radiation synthesis of metal nanoparticles, for free use of any lab in the Member States, increased experience, skills and confidence of the participating laboratories in planning and performing radiation synthesis as well
as in testing and characterization of the products. This will provide good basis for developing products based on metal nanoparticles.

PORTUGAL

NANOSTRUCTURED HYBRID MATERIALS BY RADIATION PROCESSING ASSISTED BY IONIC LIQUIDS

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Abstract

Hybrid materials (HMs) are a class of materials that enable the integration of organic and inorganic characteristics at the molecular level in a single material. Consequently, they have a wide range of high demanded possible applications, namely as biomaterials, anti-corrosion coatings and as a surface modifiers of fabrics.

The radiation processing of this type of materials is already an alternative to the current sol-gel process, given opportunity to the development of different properties and functionalization’s not easy to access through the traditional way of preparation. Bioactive PDMS-TEOS-ZPO (polydimethylsiloxane - tetraethylortosilicate - zirconium propoxide) hybrid materials for biomedical applications (bone cements) and with biocide activity are successful examples of HMs prepared through gamma irradiation. Although, the severe conditions of radiation processing (high dose-rates and absorbed doses) needed for the preparation of hybrid materials confine the possibilities to go further in the development of new properties and functionalization’s of these type of nanostructured materials.

The introduction of ionic liquids (ILs) in HMs precursor’s composition could be a solution to overcome this problem. Their special capability to dissolve, at the same time, both organic and inorganic solutes assisting the copolymerization reaction of the PDMS could be of crucial importance in a synthesis involving TEOS/ZPO and PDMS. Our main objective is thus to test a new approach in the radiation processing of nanostructured HMs taking advantage from the “best of two kingdoms”: ionizing radiation and ILs. The influence that ILs cause in the necessary doses, dose rates and specific conditions of irradiation will be studied in order to make specific tailored hybrid materials more accessible and affordable. Simultaneously, the development of high demanded and/or special functionalization’s will be considered, trying to extend by this way the range of applications of this type of materials.

1. OBJECTIVE OF THE RESEARCH
This project aims to carry out a systematic study over the influence of the addition of ionic liquids (RTIL – room temperature ionic liquids) to the hybrids’ precursors mixture, on the irradiation conditions for preparation of PDMS-based ormosils and its effects on their nanostructure. The research will also pay close attention to the optimization and development of new properties as so to explore the possibilities of efficient new functionalization’s of this materials, in order to expand their range and specificity of applications; (e.g. control of porosity and surface roughness for adequate vascularization and cell anchoring/proliferation processes, are important parameters for osteointegration of bone implants).

2. INTRODUCTION

Hybrid materials are a class of materials that enable the integration of organic and inorganic characteristics at the molecular level in a single material. In this way materials with unusual optical, mechanical or even bioactive properties are obtained, which are especially suitable for applications as sensors and bio-sensors, non-linear optical (NLO) materials, lasers, selective membranes, catalysts and protective coatings. Due to these features and to their wide range of hide demanded possible applications namely as biomaterials [1], anti-corrosion coatings [2] and as a surface modifier of fabrics [3], the development of hybrid materials has become one of the fastest R&D areas [4]. Ormosils (organic modified silicates) are a special class of nanostructured hybrid materials in which the organic compound is chemically bonded to a silicate network.

The preparation of hybrid materials is carried out normally by the well-established sol-gel process, usually through the alkoxides method that leads to high purity products at relatively low temperatures. This involves the mixing of a polymer with a metal alkoxide and subjecting the mixture to hydrolysis and condensation reactions followed by gelification.

Polydimethylsiloxane-silica (PDMS-SiO2) based hybrid materials prepared by this way have been widely explored for the production of biomaterials thanks to natural PDMS properties (optically clear, inert and non-toxic). Actually, ormosils of PDMS-TEOS (tetraethylortosilicate) have been produced with quite different properties ranging from those of characteristics of conventional glasses to those typical of flexible materials (elastomers) and, obviously with a wide range of applications: scaffolds for bioreactors [5,6], tissue engineering [7, 8] and drug delivery systems [9, 10].
Hybrids were found to have higher mechanical and thermal stability when crosslinked polymers are formed, presenting higher robustness and decomposition temperatures than those with linear polymers. Based on this fact a new method for the preparation of these materials based on gamma irradiation of the precursors mixture with no addition of any other chemical compound was developed at C²TN/IST. The starting point was the fact that the polymer crosslinking can be easily achieved by gamma irradiation [11]. The team involved in these studies have been particularly interested in the reactional ternary system PDMS-TEOS-ZPO (zirconium propoxide), due to the good properties of PDMS not only as a resource for the preparation of biomaterials but also for the development of compatible organic-inorganic materials for conservative processes of stone-based cultural artefacts.

It should be noted that the gamma irradiation method developed has been shown to be particularly suitable for the preparation of hybrids for biomedical applications as it provides the possibility to obtain sterilized materials at one single step and free of chemical products other than those derived from the precursors. In parallel it overcomes the extra-long aging and drying times required by sol-gel process (in some cases can be extended beyond a month) [12].

The effect of the PDMS molecular weight (Mw), ZPO content, precursor’s ratio and irradiation conditions on the microstructure and properties of the hybrids are now well understood and documented [11, 13-16]. The microstructure of PDMS-TEOS-ZPO hybrids obtained by the method developed consists of inorganic clusters interconnected by polymer structures: these clusters develop predominantly by monomer-cluster growth from the inorganic precursors (TEOS and ZPO) as they condense on reactive sites [13, 15]; the irradiation of PDMS promotes crosslinking of its chains with the evolution of gases such as methane, ethane and hydrogen. As PDMS is silanol terminated (Si-OH) high reactive OH radicals are formed [17].

The radiation doses of preparation vary from 230 to 880 kGy, as a function of the Mw(PDMS) and the components ratio, and the system is not too much dependent on the dose rate of irradiation. The acquired experience/knowledge allow us now to prepare and functionalize PDMS-based ormosils by gamma irradiation for distinct applications: bioactive hybrid materials for biomedical applications (e.g. bone cement additives) and biocide hybrid materials as consolidants for stone-based cultural heritage artefacts.
Even though the good properties and performance of the materials obtained by the method developed, the high doses of radiation required for its preparation are a handicap that must be overcome. The principal consequences from this issue are: i) long times of irradiation that restricts the availability of irradiation services and enhances too much the final price of the materials; ii) high degradation of the samples irradiation containers, fact that restricts the success of its preparation; iii) problems of packaging integrity in the case of sterilized samples, iv) the functionalization of the materials it is conditioned by the required high level of radiation absorbed doses of preparation, which limits the use of some radiosensitive additives and the range of polymer Mw (for properties tailoring purposes: e.g. porosity, flexibility).

The use of ionic liquids (IL) in polymer science is being reported with increasing success, including in radiation processing for advanced polymeric materials [18]. Ionic liquids are ionic salts that are liquids below 100ºC. Some of them are liquids even at room temperature (RTIL – room temperature ionic liquids). They are characterized by several properties that make them particularly useful in synthesis involving polymers: low melting point, a large liquidus range (often more than 200 ºC) a high thermal stability, a large electrochemical window (> 2 V), a large dissolution capability for many organic compounds and a negligible vapor pressure [19, 20]. Namely, the negligible vapor pressure ensures that, contrary to classical solvents, they won’t develop pressure during irradiation on confined spaces and the increased solubility allow to work in concentration ranges not possible with other solvents. In addition, hydrophobic ionic liquids will have two moieties in their constitution: a cationic/anionic area around the charges and an “organic” area near the organic tails of the cation/anion. This special capability made it possible to dissolve, at the same time, both organic and inorganic solutes which could be of crucial importance in a synthesis involving TEOS/ZPO and PDMS.

This project intends to test a new approach in the radiation processing of nanostructured hybrid materials taking advantage of the “best of two kingdoms”: ionizing radiation and ionic liquids. The influence that IL’s cause in the necessary doses, dose rates and specific conditions of irradiation will be studied in order to make specific tailored hybrid materials more accessible and affordable. Simultaneously, the development of high demanded and/or special functionalizations will be considered, trying to extend by this way the range of applications of this type of materials.
3. INSTITUCIONAL FRAMEWORK OF THE PROJECT

The team involved in this project belongs to the $C^2TN$ - Centro de Ciências e Tecnologias Nucleares (Centre for Nuclear Sciences and Technologies), a research unit of Instituto Superior Técnico (IST), Universidade de Lisboa.

$C^2TN$ performs R&D, Advanced Training & Education, Consulting and Services in Nuclear Sciences and Technologies, aiming to be a strategic Unit for the Portuguese R&D and innovation policies in this area. The quality of the research done at $C^2TN$ was recognized as Excellent by the national funding agency (FCT – Fundação para a Ciência e Tecnologia) in the latest evaluation exercise (2015-2020).

The campus where it is inserted own an Ionizing Radiation Facility (with an experimental Co-60 source (2.1 kCi; Mar-2019) and a linear accelerator), and a semi-industrial Co-60 facility (142 kCi; Mar-2019), UTR; unique in the country, as well as other laboratories and important analytical techniques.

Over the last years our research group has gained a consistent experience in distinct research areas such materials sciences, ionizing radiation processing, radiomicrobiology, biology sciences, CH conservation techniques and nuclear analytical techniques for elemental and isotopic determinations, constituting a competent team in Materials Science, Environment and Cultural Heritage area.

The team of Advanced Materials of our group has been focus mainly on the development and optimization of new, modified and/or functionalized polymeric and hybrid materials, using radiation processing techniques. Research in hybrid materials has been centered mainly on the development and optimization of an alternative method, by gamma irradiation, for the preparation of polydimethylsiloxane-tetraethylorthosilicate (PDMS-TEOS) for bone reparation/regeneration or as a part of bone cements composition.

Recently we have been particularly involved in the preparation of ormosils with biocide content, by ionizing radiation techniques, which could be used alone or as additives to the existent composite materials used in conservation processes of ancient stone-based artefacts (e.g. Roman mosaics).
The research in radiation processing of macromolecular advanced materials involves collaborations with other important institutions:
- Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa
  Department of Chemistry
  Department of Conservation and Restoration
- University of Aveiro
  Department of Materials Engineering and Ceramics
  CICECO – Aveiro Institute of Materials
- Faculdade de Ciências, Universidade de Lisboa
  Department of Animal Biology
  Centre for Ecology, Evolution and Environmental Changes (cE3c)
- Higher School of Technology of Tomar (ESTT), Polytechnic Institute of Tomar
  Department of Archeology Conservation Restoration and Heritage (ACRP)
- Monographic Museum and Ruins of Conimbriga – National Museum
- NOVA Medical School – Faculdade de Ciências Medicas, Universidade Nova de Lisboa
- Budapest Neutron Centre (BNC), Yellow Submarine / SANS, Budapest, Hungary

4. MATERIALS AND METHODS

Materials and methods are described in the context of the tasks defined to achieve the proposed goals:

4.1. EVALUATION OF THE IONIZING RADIATION EFFECT ON IONIC LIQUIDS

Selection of a consistent and efficient group of IL’s, with a good chemical compatibility with the organic and inorganic nature of the PDMS-based hybrids precursors and simultaneously with a good resistance regarding ionizing radiation. The toxicity, biocompatibility and biodegradation of the ILs to use will be another important concern in the selection process.
The initial group of ILs to study includes: EMIM OAc (1-Ethyl-3-methylimidazolium acetate), EMIM Cl (1-ethyl-3methylimidazolium chloride), biocompatible ILs of Cholinium amino-acids ionic liquids ([Ch][AA] Ils) group [21], and Cholinium-derivative-based ionic liquids.

![Chemical structure of EMIM OAc, EMIM Cl, and Cholinium amino-acids ionic liquids.](a) (b) (c)

**FIG 1**: Chemical structure of (a) EMIM OAc (1-ethyl-3-methylimidazolium acetate), (b) EMIM Cl (1-ethyl-3methylimidazolium chloride) and (c) Cholinium amino-acids ionic liquids ([Ch][AA] Ils).

The ILs will be irradiated (gamma or/and e-beam) with increasing absorbed doses, in the same experimental conditions (dose rate, irradiation environment) defined in the preparation method of PDMS-based hybrid materials already developed, in order to determine their radio-resistance/radio-degradability.

The following analytical techniques will be used as necessary for the characterization of the irradiated ILs: FTIR, Thermal Analysis (DSC and TGA), elemental analysis and chromatography.

These studies will be conducted using the irradiation facilities (IRIS and/or UTR) at CTN/IST, and all the analysis will be performed at C²TN/IST laboratories.

**NOTE**: All the irradiation assays needed in the framework of this project will be controlled by routine dosimetry through PMMA dosimeters from Harwell (Amber and Red Perspex).

4.2. EVALUATION OF THE ILs EFFECT ON THE RADIATION DOSE OF PDMS NON-FLOWING GEL POINT

PDMS non-flowing gel point is obtained with an absorbed dose near 320 kGy (irradiation in absence of air). The crosslinked PDMS obtained by this way is a flexible, transparent and
hydrophobic material with a high temperature of degradation. Thus, so, the objective in this task is to evaluate, from the ILs’ previously selected, which of them interfere positively in PDMS crosslinking reaction, reducing the irradiation dose to attain its non-flowing gel point. Different doses of irradiation and PDMS/ILs ratios will be studied.

Once again, the irradiations will be done at our irradiation facilities, in the same experimental conditions of the preparation protocol developed for PDMS-based hybrid materials.

The characterization of the irradiated PDMS crosslinked in the presence of the selected ILs will be done at C²TN laboratories. Analytical techniques such as FTIR, DSC, TGA, contact angle and common chemical techniques (soxhlet extraction, gravimetric techniques, etc) will be used as necessary (as so others considered helpful, although not listed here), in order to access the gel state of the irradiated PDMS/ILs samples.

4.3. PREPARATION OF PDMS-BASED HYBRID MATERIALS BY RADIATION PROCESSING ASSISTED BY ILs

The objective is to obtain, in a more expeditious and affordable way, PDMS hybrid materials with improved functionalized properties to be used effectively for biomedical applications (bone cements and bioactive materials) and for other emergent applications in which the team are involved (e.g. for conservation/preservation of stone-based cultural artefacts, catalytic supports, adsorbents, etc). Simultaneously, maintaining the good properties already identified in the system PDM-TEOS-ZPO, it is planned the development of efficient alternative methods of functionalization of these type of materials.

For this purpose, will be essential our previous experience in the preparation of hybrid materials by gamma irradiation: the behaviour of the precursors to be used (PDMS, TEOS and ZPO) face to ionizing radiation, their concentrations ratios as so the irradiation parameters.

The basic steps of the method developed at C²TN consists in the direct irradiation of the precursors, at nitrogen atmosphere, followed by PDMS solvent evaporation, washing in PDMS solvent in order to assure that free PDMS chains are removed, and again subjected to solvent evaporation (see FIG.2). Total dose of irradiation is controlled based in the dose to achieve the non-flowing gel point of PDMS, which depends on Mw (PDMS).
FIG. 2. Diagram of the experimental protocol for the preparation of hybrid materials through gamma irradiation.

i) Batches of PDMS hybrid materials with compositions already tested will be prepared by this way to serve as reference materials;

ii) New batches of PDMS/IL hybrids will be prepared taking this protocol as reference: ILs selected will be introduced in the precursor’s composition and the mixtures irradiated according to the protocol above described. Different composition ratios absorbed doses and dose rates of irradiation will be tested regarding the reactional efficiency and the final properties of the materials obtained.

4.4. PHYSICO-CHEMICAL AND STRUCTURAL CHARACTERIZATION OF THE NEW PDMS/ILs-BASED HYBRIDS’

To obtain new hybrid materials with adequate properties which satisfy effectively the demands for the intended applications will be necessary a continuous process of analysis of the new prepared materials (PDMS/IL hybrids) in order to allow the optimization of their properties/functionalization/behavior as a function of the IL used and the respective ratio in the precursor’s mixture.

With this purpose, the new materials prepared will be exhaustively and systematically characterized. The following analytical techniques will be used as necessary for the elemental, morphological, mechanical, structural stability and their chemical nature characterization: XRD, XRF, PIXE (by nuclear micro-beam techniques), optical microscopy and SEM, DSC, TGA, FTIR,
PALS, contact angle measurement, mechanical assays (all these techniques are available at C²TN/IST).

Effects of the new methodology of preparation on the nanostructure of the hybrids will be evaluated by SANS analysis (Budapest Neutron Centre (BNC), “Yellow Submarine”).

Hybrid materials obtained by this new approach will be compared with batches of samples obtained in the same conditions (composition ratio and irradiation conditions) but without the addition of ILs’ to the precursor’s mixtures.

NOTE: In the case of PDMS/ILs-hybrids prepared or intended for biomedical applications, if temporary possible, they will be tested regarding their toxicity; (these assays can also be performed at our laboratories).

4.5. OPTIMIZATION OF THE METHODOLOGIES FOR THE PREPARATION OF PDMS-HYBRID MATERIALS BY RADIATION PROCESSING ASSISTED BY ILs

Precursors/ILs concentration ratios, dose rate of irradiation, absorbed dose of preparation, and other irradiation or reactional parameters will be subject to systematic analysis aiming the optimization of the preparation methodologies as a function of the properties intended in the hybrid materials produced.

4.6. PHYSICO-CHEMICAL AND STRUCTURAL FUNCTIONALIZATION OF PDMS-HYBRIDS FOR SPECIFIC APPLICATIONS THROUGH THE NEW DEVELOPED METHODOLOGY

The purpose is to explore new possibilities of functionalization of the PDMS- based hybrids for specific applications (mainly for biomedical and environmental applications) through ILs assisted ionizing radiation processing. The possibility to tailor properties just like i) porosity and porous structure; ii) surface roughness; iii) gel fraction; iv) gases permeability; v) biocompatibility; vi) bioactivity; vii) biocide activity, and viii) degradability, through the use of the adequate IL enlarge the frontier of applications of these fantastic class of materials.
5. WORK PLAN

The work plan of this proposal involves six tasks, which intends to attain six specific objectives:

1- Selection of an efficient and toxicologically safe group of the most adequate and promising ILs, regarding the chemical nature of the precursors (chemical compatibility) and the intended final nanostructure of the hybrids.

2- Evaluation of the ionizing radiation effected on the selected ILs.

3- Evaluation of the ILs effect on the radiation dose to attain PDMS non-flowing gel point.

4- Definition of new irradiation parameters and optimization of the preparation method of PDMS-based hybrids by radiation processing assisted by ILs.

5- Evaluation of the effect of the ILs on the molecular structure of the new hybrids and consequently on their final properties.

6- Explore new possibilities of functionalization of the PDMS-hybrids for specific applications (mainly for biomedical and environmental applications) by radiation processing assisted by ILs.

The Tasks, already introduced and described in the Materials and Methods section of this document, are:

Task 1: Evaluation of the ionizing radiation effect on ILs (6 months);

Task 2: Evaluation of the ILs effect on the radiation dose of PDMS non-flowing gel point (6 months);

Task 3: Preparation of PDMS-based hybrid materials by radiation processing assisted by ILs, (12 months – in parallel with Task 3);

Task 4: Physico-chemical and structural characterization of the new PDMS/ILs-based hybrids (12 months – in parallel with Task 3);

Task 5: Optimization of the methodologies to prepare PDMS-hybrid materials by radiation processing assisted by ILs (5 months);

Task 6: Physico-chemical and structural functionalization of PDMS-hybrids for specific applications through the new developed methodology (7 months).
5.1. PROJECT TIMELINE

In the project timeline of 4 years, the tasks described above will be sequenced as follows:

- **1st year**: Task 1 (6 months) and Task 2 (6 months). Work on Task 2 will be performed once Task 1 is finished.

- **2nd and 3rd years**: Task 3 (12 months) and Task 4 (12 months). These 2 tasks will be performed almost in parallel once the results from Task 3 are delivered in Task 4 and, the data obtained in Task 4 will feed Task 3 for the adequacy of the preparation method being developed (depending on the properties observed in each new batch of hybrids’ samples prepared). Either so, these two tasks will be active almost up to the end of the project.

- **4th year**: Task 5 (5 months) and Task 6 (7 months). Work on Task 6 will be performed once Task 5 is finished.

TABLE 1 and 2 summarizes the above description.

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<th>TABLE 1: PROJECT TIMELINE FOR THE 1ST AND 2ND YEARS.</th>
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<td>TASK 2</td>
<td>Evaluation of the ILs effect on the radiation dose of PDMS non-flowing gel point (6 months)</td>
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<tr>
<td>TASK 3</td>
<td>Preparation of PDMS-based HMs by radiation processing assisted by ILs (12 months - in parallel with Task 4)</td>
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<td>TASK 4</td>
<td>Physico-chemical and structural characterization of the new PDMS/ILs-based hybrids (12 months - in parallel with Task 3)</td>
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<td>TASK 5</td>
<td>Optimization of the methodologies to prepare PDMS-hybrid materials by radiation processing assisted by ILs (5 months)</td>
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<td>TASK 6</td>
<td>Physico-chemical and structural functionalization of PDMS/ILs-hybrids for specific applications through the new developed methodology (7 months)</td>
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5.2. WORK PLAN FOR THE FIRST YEAR

In the first year of the project, the team will be focus on three main subjects:

1- Selection of a consistent and toxicologically safe group of the most adequate and promising ILs, regarding the chemical nature of the hybrids precursors (chemical compatibility) and the intended final nanostructure of the hybrids;
2- Evaluation of the ionizing radiation effect on the selected ILs;
3- Evaluation of the ILs effect on radiation dose to attain PDMS gel-point.

These 3 issues are considered in Task 1 and 2 already described. Summarizing:

- The objective of Task 1 is to select a consistent and efficient group of 3-5 ILs, with a good chemical compatibility with the organic and inorganic nature of the PDMS-based hybrids precursors (PDMS, TEOS and ZPO) and simultaneously with a good resistance regarding ionizing radiation. The toxicity of the ILs to use will be another important concern in the selection process.

The initial group of ILs to study includes: EMIM OAc (1-Ethyl-3-methylimidazolium acetate) and Cholinium amino-acids ionic liquids, which are described in literature as being ILs with low toxicity and biodegradable.

The ILs will be gamma irradiated with increasing absorbed doses, in the same experimental conditions (dose rate, irradiation environment) defined in the preparation method of PDMS-
based hybrid materials already developed by the team, in order to determine their radio-
resistance. If possible, the team would like also to reproduce this study by e-beam irradiation.

The following analytical techniques will be used as necessary for the characterization of the
irradiated ILs: FTIR, Thermal Analysis (DSC and TGA), RMN and Nuclear Microprobe
(PIXE, RBS, STIM) for elemental analysis.

These studies will be conducted using the irradiation facilities (IRIS and/or UTR) at CTN/IST,
and all the analysis will be performed at C²TN/IST laboratories.

- In Task 2 the objective is to evaluate, from the ILs selected in Task 1, which of them, and in
which conditions, interfere positively in PDMS crosslinking reaction, reducing the radiation
dose to attain its non-flowing gel point. It is also desirable that i) ILs do not markedly alter
the structure and matrix properties already identified in the pure PDMS crosslinked without
addition of ILs, and ii) the crosslinking reaction maintains itself almost independent of the
irradiation dose rate.

Different dose-rates, doses of irradiation and PDMS/ILs ratios will be studied.

Once again, the irradiations will be done at our irradiation facilities, in the same experimental
conditions of the preparation protocol developed for PDMS-based hybrid materials.

The characterization of the irradiated PDMS crosslinked in the presence of the selected ILs’
will be done at C²TN laboratories. Analytical techniques such as FTIR, DSC, TGA, contact
angle and common chemical techniques (soxhlet extraction, gravimetric techniques, etc) will
be used as necessary (as so others considered helpful, although not listed hear), in order to
access the gel state of the irradiated PDMS/ILs samples.

NOTE 1: All the irradiations will be performed at our irradiation facilities (IRIS and UTR), using
irradiation geometries previously characterized by Primary Dosimeters (Fricke and Ceric-Cerous).
Samples absorbed dose will be measured through routine dosimetry using calibrated Harwell
Dosimeters (Red and Amber Perspex).

NOTE 2: If possible, the team would like also to reproduce this study by e-beam irradiation.
NOTE 3: Laboratorial infrastructures, experimental resources as so the analytical techniques described will be used as necessary. Although, the work plan is not closed to new approaches whenever they prove to be valid and important to achieve the proposal objectives.

5.3. EXPECTED OUTPUTS

Expected outputs in the course of the implementation of the proposed work program include:

1\textsuperscript{st} year:
- To obtain a selected group of ILs with proven chemical compatibility with the group of precursors (PDMS, TEOS and ZPO) used, and kinetically efficient in terms of irradiation parameters;
- Evaluation of the effect of the most promising ILs \textit{i)} on the radiation dose to attain the PDMS non-flowing gel point, and \textit{ii)} on the properties of the pure PDMS crosslinked by irradiation in their presence.

2\textsuperscript{nd} and 3\textsuperscript{rd} years:
- New batches of PDMS/IL-based hybrids obtained through radiation processing.
- Physico-chemical characterization of the batches of PDMS/IL-hybrids prepared.
- Comparison of the properties of the hybrids obtained by the two methods: irradiation of the precursors without and with ILs.

Special efforts will be done in order to obtain clear evidences about the molecular organization of the hybrids prepare through the new methodology. The maintenance of the characteristic hybrid nanostructure must be assured.

4\textsuperscript{th} year:
- Optimized protocols for the preparation of PDMS-hybrid materials by radiation processing assisted by ILs.
- Nanostructured PDMS/IL-hybrids obtained through the new optimize protocols.
- Preliminary tests of PDMS/IL-TEOS-ZPO hybrids functionalized for biomedical applications and for conservation/preservation of stone based artefacts.

6. RELATED WORK ALREADY PERFORMED OR IN PROGRESS

The team involved in this proposal has already developed a solid know-how and possesses a large experience in a wide range of techniques, constituting a competent team in Nuclear Physics and Chemistry, Radiation Technologies, Environment and Materials Science. All the sensitive areas of scientific knowledge required for the proper and responsible implementation of the project are addressed: preparation of polymeric and hybrid materials by irradiation techniques, physico-chemical, mechanical and structural characterization regarding its adequacy or functionalization for specific practical applications.

i) Regarding the radiation processing of polymers assisted by ILs, members of the present team have already reported successful work, about the synthesis of novel gamma-induced porous PHEMA-IL (BMIPF₆) composites with ionic conductivity [22]. The optimization of the preparation method to electrochemical applications of these composites is currently ongoing.

ii) Work on the characterization and use of ILs on environmental applications is ongoing at C²TN, involving members of this project team [23–25].

iii) Regarding this project there are to mention that the kickoff meeting with all the members of the research team has already taken place on the beginning of February 2019. The first Task defined on the work plan have already started:

- Three ionic liquids were selected and acquired for the first irradiation assays:
  - EMIM OAc (1-Ethyl-3-methylimidazolium acetate),
  - EMIM Cl (1-ethyl-3methylimidazolium chloride) and
  - Chol OAc (Cholinium acetate).

- A new irradiation structure and respective samples holder was projected, constructed, and mounted on the Co-60 facility (UTR) for the irradiations projected (see FIG. 3). The dosimetric characterization of this new irradiation geometry was already performed.
7. CONCLUSIONS

The present research plan will be able to highlight the potential of the symbiosis between radiation processing and ionic liquids in the processing and development of nanostructured materials. The proponents of this project believe that this is a consistent and feasible approach to optimize the preparation of hybrid materials through ionizing radiation techniques, extending the possibilities of functionalization and, consequently, the range of applications of this type of materials.

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DEVELOPMENT OF NEW APPROACH TO FABRICATION AND MODIFICATION OF NANOSTRUCTURES AND NANOHYBRID MATERIALS USING X-RAY IRRADIATION

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Abstract.
The radiation-chemical methods for synthesis of nanomaterials are commonly based on using γ-rays or e-beams. In this paper we highlight the potentiality of a novel approach using relatively soft X-rays (10 – 50 keV) for generation and modification of metal nanostructures in polymer matrices, which can be useful for various technological applications. The key point of this approach is selective absorption of the X-ray photons by heavy elements, which provides strong local enhancement of the radiation-chemical processes in the vicinity of metal clusters and nanoparticles dispersed in an organic or polymer medium. The effect may be tuned due to variations in nanoparticle size, photon energy and system organization. The approach is illustrated by several recent examples and possible prospects are discussed.

1. Introduction
The radiation-chemical methods provide wide opportunities for synthesis and modification of nanostructured functional materials for various demanding applications, including ultrafine filters, catalysts, sensors, lithographic resists, materials with specific optical and magnetic properties, antimicrobial compositions, etc. These methods can be considered as green and economically competitive alternative to conventional chemical technologies [1]. Generally speaking, the radiation chemistry makes use of both “top-down” and “bottom-up” approach in nanotechnology as well as their combinations. The former approach is related to the so-called “track technologies” [2] and lithography [3], whereas the latter one is particularly useful for production of nanogels [4], metal nanoparticles [5] and polymer-based nanohybrid (or nanocomposite) materials [6]. Among other nanostructured systems, the latter materials exhibit unique combination of properties for very diverse applications. In particular, the metal-polymer nanohybrids may act as catalytic systems, nonlinear optical devices, magnetic materials, biosensors and antimicrobial coatings. Also, some oxide-polymer nanohybrids may exhibit useful functional properties (mechanical, magnetic, and electronic). A specific case is represented by biocompatible protein-based nanohybrids containing metal nanoparticles, which may be considered as promising systems for teranostics [7].

From technological point of view, most common procedures for radiation-chemical synthesis of nanohybrids (as well as other kinds of “bottom-up” radiation nanotechnologies) are based on using γ-rays or e-beams. Application of γ-irradiation from $^{60}$Co isotope sources typically provides highly uniform dose distribution and relatively low dose rate leading to formation of uniformly distributed nanoparticles in polymer matrixes. On the other hand, using e-beam sources makes it possible to control the size and spatial distribution of nanostructures due to variations of beam energy and absorbed dose rate. Meanwhile, if we consider the basic nanoscale physics lying behind these two
kinds of processes, it is rather similar. Indeed, in both cases the radiation-chemical processes are induced by secondary electrons, which are generated either by high-energy photons through Compton mechanism (in the case of γ-rays) or by fast primary electrons through inelastic scattering (in the case of e-beams). The energy and spatial distribution of secondary electrons is qualitatively similar in both cases; furthermore, it is not particularly sensitive to the system composition. Therefore, the type of radiation source affects mainly macroscopic parameters of the process (due to difference in penetration depth of radiation) and kinetics of secondary chemical reactions (due to difference in the intensity and, respectively, absorbed dose rate). However, the situation becomes different at physical level, if one considers the action of X-rays with the energy between 10 and 100 keV. In this energy region the most important mechanism of primary photon interaction with matter is photoelectric absorption (photoeffect) and the cross-section of this interaction is very sensitive to the absorber nature. In case the photon energy is above the K-edge of the absorber atoms, the atomic absorption cross section is roughly proportional to $Z^4$ and the mass-absorption coefficient ($\mu_{en}/\rho$) is proportional to $Z^3$ (where $Z$ is an absorber atomic number). This feature provides a basis for particularly efficient radiation-chemical modification of the systems containing heavy elements with $Z > 20$ (like transition or noble metal atoms) and leads to a specific effect of strong local intensification of the radiation-chemical processes in the interface regions of nanostructured systems. In our recent studies we have demonstrated the applications of X-ray irradiation for preparation of metal-polymer nanohybrids with different size and spatial distribution of nanoparticles from swollen polymer films [8-10], solutions [11], and suspensions [12].

In this report we present the most recent results illustrating applications of X-ray irradiation for films and thin coatings and outline the prospects of this novel approach for manipulations with the nanostructure design, which can be used for production of nanohybrid materials with specific localization of nanoparticles as well as for modification of biocompatible protein-based nanosystems.

2. Experimental design and methods
The approach to fabrication and modification of metal-polymer nanohybrid using X-ray irradiation developed in the Laboratory of High Energy Chemistry (LHEC) in Lomonosov Moscow State
University is based on powerful (5 kW) X-ray irradiators equipped with the 5BKhV-6(W) tubes with tungsten anodes. The applied voltage can be tuned between 14 and 50 kV. The samples in the form of solutions, suspensions, or swollen polymer films are typically irradiated in thin-wall plastic cells positioned close to the output window of the X-ray tube. The absorbed dose rate calibrated with ferrosulfate dosimeter is ca. 5 to 20 Gy/s. However, the actual absorbed dose rate in the samples containing large amounts of metal ions can be several times higher and the local absorbed dose rate in thin films loaded with metal ions can exceed 100 Gy/s. Air cooling is applied to avoid sample heating during irradiation.

Most experimental studies were carried out using interpolymer or interpolyelectrolyte complexes (IPECs) with metal ions, which are known to be uniquely suitable precursors for metal-polymer nanohybrids [13]. In particular, the poly(acrylic acid) (PAA) – polyethyleneimine (PEI) interpolyelectrolyte complexes combine high ion sorption capacity, good dialysis permeability, and strong interactions with partially charged metal surface, which is very important for efficient radiation-induced synthesis of both noble and transition metal nanoparticles embedded in the polymer matrix [8-10, 13]. Other types of polymers used were polyallylamine [12, 14], poly(vinylimidazole) (joint studies with the group of Prof. O.Güven, Hacettepe University, Turkey), poly(1-vinyl-1,2,4-triazole) [15], and poly(styrenesulfonic acid).

A common procedure of the radiation-chemical synthesis of metal-polymer nanohybrids by reduction of metal ions developed in our laboratory is based on using water-ethanol mixture (10 wt% C₂H₅OH) as a reaction medium. Basic scheme of the radiation-induced synthesis of nanoparticles through reactions of metal ions with intermediating resulting from the medium radiolysis can be described by the following reaction scheme [5, 16].

\[
\begin{align*}
H_2O & \rightarrow e_{aq}, OH^-, H^+, H_2, H_2O_2 \\
e_{aq} + M^{x+} & \rightarrow M^{(x-1)+} \\
CH_3CH_2OH + OH^- & \rightarrow CH_3'CHOH + H_2O \\
CH_3CH_2OH + H^- & \rightarrow CH_3'CHOH + H_2 \\
Me^{x+} & \rightarrow Me^{(x-1)+} \rightarrow \cdots \rightarrow Me^0 \\
Me^0 + Me^{x+} & \rightarrow Me_2^{x+} \rightarrow Me_m^{x'}
\end{align*}
\]
CH\textsubscript{3}CHOH + Me\textsubscript{m}\textsuperscript{y+} → CH\textsubscript{3}CHO + Me\textsubscript{m}\textsuperscript{(y-1)+}

Me\textsubscript{n}\textsuperscript{x+} + Me\textsubscript{m}\textsuperscript{y+} → Me\textsubscript{n+m}\textsuperscript{(x+y)+}

It should be noted that the transport of reductive species is of primary significance for heterogeneous systems (like swollen IPEC films). The kinetics of metal ion reduction under irradiation was monitored by EPR and optical (UV-visible spectroscopy) and the formation of metal nanoparticles was revealed by surface plasmon absorption manifested in the optical spectra. Transmission electron microscopy (TEM) was used to reveal the nanoparticle localization and size distribution in the resulting nanohybrid materials. X-ray diffraction (XRD) was applied to determine the characteristics of metal lattice in nanoparticles. In some studies, FTIR spectroscopy was also used to monitor the chemical changes in matrix resulting from irradiation (these changes were found to be relatively minor, or, at least acceptable in most cases).

3. Concept of radiation-chemical contrast

As mentioned in the Introduction, the most important feature of X-ray absorption in the energy region of several tens keV is selectivity of primary interactions for the systems containing elements with significantly different Z values. If we consider homogeneous systems (solutions or molecular dispersions), this effect will mainly result in strong radiation-chemical sensitization of organic or aqueous systems in the presence of even small amounts of heavy atoms (e.g., transition or noble metal ions). However, in the case of nanostructured systems containing heavy nanoparticles dispersed in light medium, one should expect abrupt change of the photon absorption coefficient at the interface between nanoparticle and matrix, somewhat similar to the contrast observed in the X-ray images. Secondary electrons ejected from metal nanoparticles to medium deposit their energy in a relatively small vicinity of nanoparticles. These electrons induce local enhancement of the rates of chemical reactions forming a sort of radiation-chemical contrast [9], which may be illustrated by Fig. 1.
From physical point of view, the scale of local processes and the enhancement efficiency are determined by two key factors related to nanodosimetry: (1) nanoparticle size and (2) photon energy. Regarding the first factor, on the one hand, “contrast” implies that there is an interface boundary related to the minimum size of a compact heavy nanoparticle. On the other hand, increasing the nanoparticle size results in increasing probability of absorption of the secondary electrons inside the nanoparticle, without any chemical consequences. This compromise suggests that there is an optimal diameter of nanoparticles close to the energy deposition length for secondary electrons: $d \approx l_e$ [9]. The latter value increases with the secondary electron energy and reaches ca. 150 nm for $E_e \approx 2$ keV in water [17]. This is a practical limit for nanotechnology. The second factor determines absorption cross-section and energy of secondary electrons. The most favorable conditions for manifestation of local nanoscale effects are achieved, if the photon energy is slightly above the characteristic energy (K-edge for the elements with $Z < 50$): $E_p - E_k < 2$ keV for the elements with $Z < 50$. Similar consideration may be applied to L-edge for of heavier elements. In the case of typically used white X-ray radiation (Bremsstrahlung), the numerical calculations taking into account complex dependence $\mu_{en}/\rho(E)$ and $l_e(E)$ or Monte-Carlo simulations should be generally applied to reproduce the primary distribution of radiation-chemical events, although a simplified qualitative picture can be produced analytically [9].
Depending on the energy spectrum of X-ray photons and the electronic properties of heavy element this may result in self-acceleration of the nanoparticle growth at a certain stage or production of small “daughter” metal nanoparticles leading to a very specific nanocomposite pattern [9].

In addition to physical basis of the nanoscale contrast, in the case of hybrid materials (especially, for those produced by wet technologies), one should consider diffusion of reagents (radiation-induced intermediates) and their reactivity. In particular, in swollen polymer films used as precursors of metal-polymer nanohybrids [8-10], the mobility of reactive species is changed strongly when moving from interface to the bulk region and it affects the preferential localization of the metal clusters and nanoparticles. On the other hand, the metal ions from the bulk film can migrate to the surface to fill the vacant ligand states. Actually, in such cases, one may obtain a “zone-like structure”, where the fully covered surface layer is separated from a densely populated sub-surface layer by an empty zone. An example is shown in Fig. 2.

![TEM image of a PAA−PEI−Ag⁺ sample irradiated with X-rays for 30 min (surface part) (details are given in Ref [9]).](image)

*FIG. 2. TEM image of a PAA−PEI−Ag⁺ sample irradiated with X-rays for 30 min (surface part) (details are given in Ref [9]).*

The interplay of physical and chemical factors makes it possible to generate a variety of different-type metal nanostructures in polymer matrices potentially useful as catalytic systems, bactericide and fungicide materials, and biosensors, which can be hardly obtained by other ways. Furthermore, the effect of radiation-chemical contrast may be applied for selective modification of the surface layer of the composites prepared by an independent method.
4. Production of nanoparticles in ultrathin films and coatings

Recently we applied the X-ray irradiation for the generation of metal nanoparticles in ultrathin coatings deposited on the cotton fibres using the “layer-by-layer” (LbL) technique [18]. This technique implies consequent deposition of several alternating layers of polyelectrolytes with oppositely charged ionogenic groups to produce a stable ultrathin coating, which can contain large amounts of bound metal ions. Several combinations of polyelectrolytes were tested, and the PAA-PEI pair was found the most suitable precursor for preparation of stable coatings with high concentrations of the adsorbed metal ions. Irradiation of the coated fibres containing high concentrations of absorbed metal ions with X-rays in water-alcohol medium made it possible to generate bound copper, silver, or gold nanoparticles localized in the coating (an example is shown in Fig. 3).

FIG. 3. TEM image of a five-layer PAA-PEI-Ag coating obtained by X-ray irradiation.

It is worth noting that the efficiency of radiation-induced generation of nanoparticles in the coating was quite high and the irradiation time required for preparation of nanostructure was several times smaller than that applied for relatively thick IPEC films used in our previous studies. This can be understood from the point of view of concept of radiation-chemical contrast outlined above. Indeed, the estimated local absorbed dose rates in the ultrathin coating with maximum metal load were between 70 and 700 Gy/s (depending on the metal ion nature and its content), whereas the absorbed dose in the bulk solution was below 20 Gy/s [15]. Furthermore, the metal ions localized in thin coating are easily available for the radiation-induced reducing species (hydrated electrons and alcohol radicals) coming from the outer medium.
The prepared cotton fibre with nanohybrid coating containing silver particles was tested as a bactericide material. It was shown that the material retains very good antimicrobial properties even after five washing cycles [15], which may be useful for particular applications, e.g., as a sportswear. It should be noted that this kind of coated materials obtained using a combination of LbL technique and X-ray irradiation may be of potential interest also for other applications (like sensors and biosensors).

5. A “one-pot” radiation-chemical synthesis of metal-polymer nanohybrids starting from monomer

One more recent application of the radiation-chemical approach to production of metal-polymer nanohybrids is concerned with a so-called “one-pot” synthesis based on simultaneous polymerization and metal ion reduction in solution. In this case, the precursor system contains solution of appropriate monomer containing metal ions. In the course of our joint study with the group from A.E. Favorsky Institute of Chemistry of the Siberian Branch of Russian Academy of Sciences (Irkutsk) it was demonstrated that the metal-polymer nanohybrids with gold nanoparticles with controlled size could be prepared by X-ray irradiation of dilute water-ethanol solutions containing 1-vinyl-1,2,4-triazole and chloroauric acid [19]. In this system, OH radicals and H atoms are completely scavenged by ethanol to produce hydroxyethyl radicals, which initiate the polymerization process. The monomer consumption and formation of nanoparticles was confirmed by optical absorption spectroscopy and the structure of composites was proved by TEM.

It is worth noting that the nanoparticle size can be adjusted due to variations in pH value. In the development of this work, the silver-polymer nanocomposites were obtained from the same monomer precursor using similar procedure. Generally speaking, the synthesis of such kind can be also performed using γ-rays or e-beams. However, in the case of X-ray irradiation, the polymerization rate can be strongly enhanced in the vicinity of gold nanoparticles due to the effect of radiation-chemical contrast. In addition to “single-pot” synthesis, this effect may be used for effective coating of existing nanoparticles by a polymer shell not necessary requiring polymerization in the bulk.
6. Conclusions and future research directions

Recent studies carried out in our laboratory have demonstrated that X-ray irradiation in the energy region between 10 and 50 keV provide a very efficient tool for fabrication and modification of metal nanostructures in different-type polymer matrices to produce useful materials for various applications. In certain cases, this method provides an opportunity for assembling unique structure pattern, in particular, in the surface regions of polymer films. One has a choice between starting from existing polymer or simultaneous polymerization and nanoparticle formation. The approach can be also applied for obtaining the composites containing metal oxide nanoparticles (e.g., for magnetic materials). A specific prospective application of the X-ray modification can be related to the fabrication of metal-protein hybrid nanoparticles stabilized by cross-linking. Previously γ-radiation was applied for this purpose [20], however, using X-rays with an appropriate energy may provide a new tool for more selective and efficient local modification.

Future research activity should comprise the following main directions:
- model studies for better understanding kinetics and mechanism of the X-ray-induced chemical processes leading to formation and growth of metal nanoparticles in organized systems;
- experimental investigation of the effect of X-ray energy spectrum on the efficiency of local radiation-chemical processes and spatial organization of metal nanostructures in polymer media and computations for better reproduction of micro/nanodosimetric picture in the nanohybrid systems irradiated with X-rays with different spectral distribution;
- fabrication of materials based on metallic and bimetallic nanostructures in polymer matrices by X-ray technique and testing their functional properties for specific applications;
- elaboration of the procedure for selective X-ray-induced modification of composite materials with existing metal and metal oxide nanoparticles;
- testing an opportunity to produce the stable biocompatible protein-coated metal nanoparticles using selective X-ray-induced modification.

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SERBIA

DEVELOPMENT OF HYDROGEL NANOACTUATORS BASED ON GOLD NANOPARTICLES, POLY(N-ISOPROPYLACRYLAMIDE) AND POLY (VINYL ALCOHOL) USING RADIATION TECHNOLOGY FOR SOFT ELECTRONICS

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Abstract

In this report, we highlight development of gamma irradiation technique for the synthesis of hydrogel nanocomposites based on photo-sensitive noble metal nanoparticles, synthetic and stimuli-responsive polymeric hydrogels for potential applications in the field of soft electronic. Radiation-technological platform provides a basis for sharp modification of physical and chemical properties for a wide range of advanced innovative nanomaterials. Though the field of soft electronic is still young and not very well defined, the basic guidelines were created as the consequence of the progress realized in recent years. One of the basic innovative elements is the introduction of photosensitive gold nanoparticles using a radiation-chemical "bottom up" method by controlling the final shape that can tune the optical properties of hydrogel nanocomposites, and as a consequence their photo-thermal capacity. First of all, modification of the shape of gold nanoparticles under different γ-irradiation absorbed dose, dose rate, capping agents and type of metal precursors, lead the obtaining of more effective soft actuator for potential application in electronics. In order to complete soft electronic requirements, γ-irradiation method is very suitable for manipulating properties of transparent hydrogel nanoactuators (shape of nanoparticles, crosslinking degree, porosity, programmable local thermo-responsive deformation) and activating of poly(vinyl alcohol) hydrogel by embedding gold/poly(N-isopropylacrylamide) hydrogel nanocomposite filaments or layer-by-layer crosslinking strategy of active gold/poly(N-isopropylacrylamide) layer crosslinked with passive poly(vinyl alcohol) layer. Current aspects of photothermal modulation based on radiation nanotechnology include development of nano-electrically functionalized network, providing bending movement of hydrogel nanoactuators.

1. OBJECTIVE OF THE RESEARCH

The major concept behind this proposal is to design innovative photothermal hydrogel nanocomposites based on gold nanoparticles, poly(N-isopropylacrylamide) and poly (vinyl alcohol) for soft electronics.
One of the basic innovative elements behind this proposal is the introduction of photosensitive gold nanoparticles using a radiation-chemical "bottom up" method by controlling the final shape that can tune the optical properties of hydrogel nanocomposites.

In order to complete soft electronic requirements, modification of the shape of nanoparticles, crosslinking degree, and porosity lead to obtain more effective soft actuator for potential application in electronics.

Gold/poly(N-isopropylacrylamide) hydrogel nanocomposite in the form of filaments will be incorporate in crosslinked PVA matrix or via layer-by-layer crosslinking of active gold/poly(N-isopropylacrylamide) with passive poly (vinyl alcohol) layer.

2. INTRODUCTION

In the field of soft electronic, power of γ-rays makes radiation technology as indispensable tool for synthesis of advanced generation of Au/nanosystems for electronic purposes. Simultaneous modification and integration of polymer/metal constituents allows fine-tuning of predefined inherent properties of the hydrogel nanocomposites, especially of biofriendly stimuli-responsive electronic devices.

Incorporation of metal photothermal nanostructures in polymer stimuli-responsive matrix has recently been widely used in electronics [1, 2]. Among different nanomaterials, nanocrystalline gold has been shown to be the most effective activator for volume reduction movement of thermo-sensitive polymers, above the lower critical solution temperature (LCST), with ability to improve mechanical properties of actuators [3, 4]. A major breakthrough of radiolytic method is possibility to produce nanoparticles and control crosslinking of polymer by simply exposing polymer molecules and metal ions dissolved in water, to γ-rays. Radiation processability is reflected on the possibility to change their properties from bulk to photothermal activity to achieve bending motions of actuators upon light exposure. The radiolytically generated active species in water, such as hydrated electrons and transient radicals, exhibit strong reduction potentials which can reduce metal ions at each encounter. Moreover, due to its ability in fine-tune dose of radiation, this method can offer good control over the morphology and size distribution of metal nanoparticles.

The formation of gold nanoparticles (AuNPs) under the action of γ-radiation is carried out through the reduction of metal ions by hydrated electrons and secondary reducing species formed by the
process of radiolysis of water. The very fast interactions of ions with metal atoms play an important role in the cluster growth mechanism. The rate of nucleation, growth and shape of metal nanoparticles can be kinetically controlled by using capping reagents, appropriate absorbed dose, organic or inorganic templates. It is known that the size of the nanoparticles decreases with increasing radiation dose rate. At high rates of radiation dose, when the number of nucleation events is much greater than the number of unreduced metal ions, smaller size of particles are obtained by the radiolytic method. On the other hand, at low dose rates, when the concentration of the nucleus is less than the concentration of unreduced ions, results in the formation of larger particles by the reduction of ions adsorbed on agglomerates. Slow reduction rate leads to form the large nucleated seed crystals and also isotropic growth on all facets resulting in large size and the quasi-spherical nanoparticles. In order to predict the shape of radiolytically synthesized nanoparticles, various methodologies have been recently developed, but overcoming surface energy to control the morphology of nanoparticles still remains a challenge.

Radiolytic, shape-controlled metallic nanocrystals including nanospheres, nanotriangles, nanorods and nanoprisms with anisotropic structure, bring up the unique photothermal effect that will significantly enhance soft electronic applications. Under the irradiation of light, local surface plasmon resonance is consequence of electrons oscillations with the frequency of the electromagnetic field that generates heat. This photothermal conversion, as a result of electron-phonon process, localized heating very fast with high selectivity [4].

Current aspects of photothermal modulation based on nanotechnology include development of nano-electrically functionalized network, providing bending movement of hydrogel nanoactuators [5]. Gold nanoparticles, as hydrogel filler, have attracted growing interest in soft electronics, due to inherent ability to transmit signals under local irradiation. Innovative functionalization of copolymer nanocomposites can be derived by radiation technology which allows a homogeneous particle size distribution with possibility to control the size and the shape of gold nanoparticles in accordance with designing human-friendly and high level ubiquitous technology that produce, interacts and consumes information [6-8]. Optimization of the parameters of radiation technology based on γ-irradiation is very important for synthesis of the hydrogel nanoactuators, to examine their electrical activity, the role of gold in the nanoparticle form, and the synergistic effect of poly(N-isopropylacrylamide)/gold hydrogel nanocomposites.
The temperature dependence of the mechanical bending deformations of hydrogel nanoactuators with tunable LCST, kinetic and thermodynamic parameters will be defined in order to comply with innovative electronic requirements of soft machine. It will be aim to align the structural properties and mechanical strength with the requirements for soft electronic [9, 10]. In order to shorten the time of optimization of the synthesis and provide a detailed insight into the mechanism of combined photothermal/bending kinetics, the concept of computational modeling for soft electronic will be applied for the first time, to overcome deformation issues and understanding activation mechanism of hydrogel nanocomposites.

3. MATERIALS AND METHODS

2.1. Materials

Poly (vinyl alcohol), PVA (medium molar mass, $M_w = 72$ kDa and min. 99% degree of hydrolysis), gold(III) chloride trihydrate, HAuCl$_4$, 2-propanol, $(CH_3)_2CHOH$ are the products of Merck, Germany. Argon, Ar, high purity (99.5%) is the product of Messer Tehnogas, Serbia. Distilled water was obtained by purifying distilled water using a Milli-Q Water System with four ion exchange columns. All chemicals used are the most readily available cleanings and are used without further purification.

2.2. Methods

Radiation-chemical synthesis of PVA-AuNPs/PNIPAM actuators will be developed by applying $^{60}$Co gamma source with nominal activity $1.8 \times 10^{14}$ Bq.
First, improving the activity of PVA-AuNPs/PNIPAM actuators will be performed by controlling the shape of nanoparticles under different dose rates (0.3kGy/h-17kGy/h) of γ-irradiation and by adding different capping agents, for its further innovative incorporation into hydrogel structure in the form of AuNPS/PNIPAM filaments in PVA hydrogels or via layer-by-layer strategy.

Designing of synergistic electrical and photothermal activity of AuNPs/PNIPAM/PVA hydrogel nanocomposites within photothermal kinetic platform will include optical, physicochemical, thermal and mechanical parameters. The maximum decrease of the size of AuNPs, along with the preferable shapes of nanoparticles with sharp corners and edges in the hydrogel nanocomposites, allows obtaining advanced photothermal properties and improving the deformation outcome of these systems for soft electronic applications.

In order to obtain materials for soft electronic application, the γ-radiation method will be use, based on the process of water radiolysis, which leads to the formation of free radicals as precursors of crosslinking process of polymer chains and synthesis of noble metal nanoparticles.

Photothermal deformation potential of novel developed AuNPs/PNIPAM/PVA hydrogel nanocomposites will be evaluated by photometric and thermomechanical analysis, and experimental obtained parameters will be used for establishing of new methodologies for modeling and simulation, required for a systematic development of soft electronic research field.
temperature and dimension measurement, and atmosphere could control components meld with powerful, flexible, software to optimize the many tests that the Q Series TMA can perform. Determination the size and shape of synthesized nanoparticles as one of the basic parameters that determine the properties of PVA-AuNPs/PNIPAM actuators, important for application (photosensitivity and effective surface area), characterization of optical and structural properties will be investigate by different spectroscopic methods. Micro-Raman spectrometer TriVista TR557 is the most flexible system for Raman and photoluminescence measurements. Three imaging corrected spectrometers of 500 and 750 mm focal length yield an excellent stray light rejection with the best resolution sharper than 0.004 nm. The optical design enables to switch between additive mode and subtractive mode without additional optics. The working range of the TR557 is from UV (185 nm) to near IR (2.2 mm), depending on the grating and detector selection. TriVista system is equipped with a CCD detector, a confocal microscope, and a software-driven XYZ stage which enables automated 3D mapping with an autofocus option. Structural properties will be investigated on the Bruker D8 Advance Diffractometer. Particle and membrane morphology will be examined by scanning electron microscopy Universal Scanning Probe Microscopy (USPM), Quesant Instrument Co.; (contact AFM, non-contact AFM, force distance curves, STM, STM spectroscopy and MFM modes). Bruker Elexsys E540 EPR spectrometer operating at X-band (9.51 GHz) with the following settings: an amplitude modulation of nearly 2 G, a frequency modulation of nearly 100 kHz, a 10 mW microwave power source, with scanning range up to 6500 G. Thermomechanical measurements will be observed by TA Instruments Thermomechanical Analyzer TMA Q400EM.

4. OUTCOMES

- Stimuli-responsive hydrogel, poly (N-isopropylacrylamide) (PNIPAM) has been extensively explored for various applications, largely due to the fact that temperature is readily to be manipulated. Enhancing the mechanical performance will extend the application area of hydrogels to soft machine. The most appealing feature of PNIPAM-based hydrogels is their volume phase transition across the lower critical solution temperature (LCST). Reducing the LCST enables operation of PNIPAM-based hydrogel
devices at lower temperature (ambient temperature) avoids the complexity of additional heating to trigger the onset of phase transition. This will extend the application of PNIPAM-based hydrogels to actuators, robotics, self-folding structures, and pattern formation. However, the use of PNIPAM hydrogels in soft electronics is generally limited by its flexibility, as well as the potential breaking and malfunctioning.

- Important approach in development application of hydrogels is improvement that is often accomplished by combining stimuli-responsive polymers with synthetic, rigid, polymers and incorporation of photothermal noble metal nanoparticles which induce mechanical reinforcement and reversible volume change transformation. In the last few decades, various approaches to radiochemical modification of stimuli-responsive polymers have been intensively investigated in order to modify their properties for specific application in electronics. Radiolytic methods based on the application of ionizing radiation (γ-radiation, electronic beams) or non-ionizing radiation have proven to be particularly suitable for the synthesis of copolymers. Radiation processability of materials is reflected on the possibility to change their properties from bulk to photothermal activity by varying the size and shape of nanoparticles, and manipulation of polymer crosslinking degree.

- Poly (vinyl alcohol) (PVA) is synthetic polymer convinient for the synthesis of the hydrogel nanocomposite, with wide application in electronics because of its mechanical stiffness. It is very suitable for the synthesis of the anticipated nanocomposite actuators because it is a water-soluble and radiation-crosslinkable polymer, optically transparent with macromolecule structure of electron donor in the reduction processing of noble metal ions. Radiation-chemically synthesized PVA hydrogels belong to rigid membranes with extremely good mechanical properties and potential electrical conductivity depending on absorbed fluid. High density of -OH group contributes to high hydrophilicity, biocompatibility and biodegradability. However, the use of PVA hydrogels in soft electronics is very significant in context of environment, safety, and health issues that are becoming an increasing focus in the electronic materials area.

- It is expected that during the development of this project, PVA-AuNPs/PNIPAM actuators will be successfully synthesized and characterized. It is also expected that different shapes and size of Au nanoparticles will exhibit wide photosensitivity potential that is optimal for soft electronic use as well as excellent mechanical bending motions, due to synergistic
Au/PNIPAM activity. According to anticipated characterization, it will be expected that correlation between observed photothermal potential of the Au nanoparticles and the mechanical properties of PVA-AuNPs/PNIPAM actuators under light exposure, bring up appropriate parameters for mathematical modeling that will be routinely applied to support the optimization of PVA-AuNPs/PNIPAM actuators.

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THAILAND

RADIATION-CONTROLLED DIVERSITY OF NANOSTRUCTURES FOR
INDUSTRIAL APPLICATIONS: COATING/PRINTINGS, COSMECEUTICALS
AND AGROCHEMICALS

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Abstract

The proposed research work is focused on nanostructure design and molecular template design for nanostructure synthesis, modification and fabrication through irradiation-induced chemical reaction techniques based on Top-down (i.e., degradation/chain scission), and Bottom-up processes (i.e., crosslinking, polymerization, grafting and reduction reaction). Single irradiation technique or combined techniques have been designed and will be developed for the preparation of a wide variety of nanostructures, such as polymer-stabilized metallic nanoparticle, core-shell hybrid nanoparticles, nanogels and core-shell polymeric nanoparticles including polymeric hydrogel template for nanostructure construction (SCHEME 1). Beside a conventional but well efficiently established process using gamma-irradiation, electron beam processing will also be emphasized for nanomaterials development for technological transformation in the future. The applications of the radiation-controlled nanostructures are focused on functional coatings/printings (e.g., superhydrophobic and antimicrobial coatings, conductive inks), cosmeceuticals (active and antioxidant nanoparticle, active compound entrapment nanoparticles) and agrochemicals (e.g., fertilizers and active compounds entrapment, moisture retention) (SCHEME 2.) Scientific approaches for the synthesis and fabrication of nanostructure by controlling parameters under irradiation process are emphasized in order to investigate and characterize using appropriated material characterization techniques. Besides scientific fundamental studies, simplying the protocol and process through simultaneous synthesis and fabrication systems will also be considered for industrial production approach. Although the synthesis and fabrication of nanostructure materials using radiation techniques have been studied and some processes have already been established, it is still important to further strengthen capacity of the effective and competitive irradiation techniques for nanofabrication of new and value-added materials for industrial applications.

1 Nanotechnology and Applications

i) Coatings/Printings: Functional coatings and high-performance inks

“Coating” is a thin layer covering on the surface of an object substrate generally applied in finishing processes for decorative appearance, information, protective barrier and functionalization “Printing” is a process for transferring or reproducing text and images to substrate surface by using a master form or template. This process is applied for decorative appearance, information, protective barrier and functionalization (e.g., super hydrophobic and antimicrobial), on to printed substrate surface. The printing process can be applied on many substrates, such as papers, boards, plastics, glass, textile etc. and it also be printed onto various shapes of the substrate either flat or preformed shapes. The overprint varnishes (OPV) or varnish is a clear transparent coating and no color material for applying to an entire substrate surface in finishing process that is a combination of oils, resins, waxes, solvents, monomer, oligomer and other materials used as to increase surface properties, for example increase of gloss for better appearance and increase of the protective barrier from abrasion and tear due to handling or contact with moisture, chemical or other potential sources of damage. Moreover, it is also referred to an
overcoating applied to a printed product following printing as finished process. Overprint is applied for entire printing surface nevertheless for only partial parts of a printed surface, it is called spot varnish. For applying OPV as coating material, the liquid varnish is formed by drying process to a solid thin layer covering on the surface of an object substrate.

Printing inks are coloured liquids or pastes, formulated to color a surface to reproduce an image, text and design. They are used to decorative appearance, information and functionalization. Printing liquid inks are applied for partial surface covering by forming solid thin layer film on the surface of substrate. The film thickness depending on the printing process used which is usually between 2 and 3 µm. Printing inks consist of dispersions of insoluble colourants (i.e, pigments) or soluble colourants (i.e., dyes) in a varnish. They are then dried forming solid thin layer film of such colourants mixture on to the substrate under printing processes. Several methods are used for drying ink on the substrate, such as absorption drying, oxidation drying, evaporation drying, chemical reaction drying (chemical cross-linking or curing) and radiation-induced drying (radiation induced cross-linking or curing). The composition of printing ink and its physical properties depend on printing process and printing surface substrate.

Basically, there are seven printing processes, i.e., i) offset lithography, ii) flexography, iii) gravure, iv) letterpress, v) screen printing, vi) ink-jet and vii) toner printing systems. For offset lithography, it uses a flat printing plate as printing template and the printing area is ink-receptive, while non-printing areas is ink-repelling. Flexography is a relief printing process that the printing areas is raised above non-printing area and the printing area receives inks from an “anilox roller”. In the case of gravure, it is the printing process that printing area is sunk into the plate (template) surface. The entire plate surface is flooded with ink and the excess ink is removed by a “doctor blade”. The remaining ink fills in the cells constructed in the plate and it is transferred to the substrate. Letterpress is a relief printing process that the printing area is raised above the non-printing area in the plate of letterpress and the plate is received ink by rollers and pressed into contact with the substrate. For screen printing, it employs a stencil principle for printing process. A rubber squeegee is used to push ink through the stencil on to the substrate. The well-known ink-jet printing process is performed through controlling the liquid printing ink droplets which then spray with high speed onto the substrate. The last toner printing systems (or known as laser printer) is an electrostatic printing process that apply powdered ink, called toner, to create printing area (an electrostatic latent image) by appropriate electrical charge and such latent image is then transferred
to the substrate and fused by heating process. The latter two processes are called “digital printing” that mean the printing process is not necessary to use real solid plate or template for printing it applies digital files as the template for printing.

Up to date, the definition of printing is not only the printing process of texts or graphics on flat (two-dimensional/2D printing) substrates, such as textiles and paper but also the deposition of a binder materials or solidifying process of materials layer by layer onto the substrate for creating a three-dimensional object. This process is called “3D printing”. Moreover, printing technique has been considered as a valuable tool for processing of functional nanomaterials. For example, in the electronics application, it can be applied for commercial mass production of nanomaterial-based printed electronics devices.

Nanomaterials are typically used in both 2D and 3D printings in order to add functionality to the polymer or multi-material systems. Nanomaterials can be applied to a polymer system for improving material properties (e.g., mechanical strength, color, flame-retardation ability, biocompatibility). Examples include the addition of clay nanoparticles to photosensitive resins to improve the mechanical properties such as impact strength for using in high-tech engineering by 3D printing. Another example is the addition of metal compounds, such as metal nanoparticles, to make conductive tracks in electronics device for 2D printing. For electronics application, nanoparticles (e.g., Au, Cu and Ag) are important role of functional materials due to their high conductivity, chemical stability, and resistance to surface oxidation. Besides, there are many conductive materials, such as conductive polymers, carbon, graphene, organo-metallic compounds and metal precursors, have been also combined into ink system to achieve conductive property. It has been reported that the addition of conductive polymers, carbon and graphene into conductive ink provided poor conductivity (10–10^2 S/cm) compared with the addition of metals (10^4 –10^5 S/cm) (Wang et al., 2016). According to nanoscale size, nanoparticles can be applied to develop conductive ink for the ink-jet printer or roll-to-roll wet coating equipment (Jung et al., 2014).

Silver nanoparticles (AgNPs) and copper nanoparticles (CuNPs) are metallic NPs generally applied for conductive inks. AgNPs are generally synthesized from Ag precursor (AgNO3) and polyvinyl pyrrolidone (PVP) stabilizer. AgNPs powder are dissolved in a general formula of ink-jet ink consisting of deionized water, ethanol, glycerol and glycol (Wang et al., 2017). CuNPs has a high conductivity similar to AgNPs but the price is inexpensive compared with AgNPs. They are
synthesized from Cu precursor (CuSO₄) using hydrazine as reducing agent and PVP as stabilizing agent via chemical reduction reaction (Li et al., 2014).

After the conductive ink containing metallic nanoparticles is formulated, it is printed on to the substrate in order to make an electronical circuit. The obtained printed circuit may be sintered by suitable sintering processes for enhancing the conductivity to approach the conductivity value of bulk metallic form.

**ii) Cosmeceuticals: Active compounds entrapment or encapsulation**

Cosmeceuticals are cosmetic products with active ingredients that is “therapeutic” benefits and mostly it refers to skin and hair care products that are a blend of cosmetics and pharmaceuticals. The advantage of cosmeceuticals is to improve the skin’s appearance and promoting healthy skin. Active ingredients can be synthetic in nature (peptides, ceramides, most vitamins), extracted and more or less purified from natural sources (botanicals, herbal extracts), obtained by biotechnology techniques such as fermentation and cell culture (enzymes and cofactors, polysaccharides and proteins), extracted from animal (including marine) sources.

The advantage of application nanoparticles for cosmeceuticals are the nanoscale of particle that able to cross biological barriers and increase the solubility of drugs and other active ingredients. Nanoemulsions, nanocrystals, micelles, polymeric nanocapsules, niosomes, liposomes, nanostructured lipid carriers, solid lipid nanoparticles, dendrimers, fullerenes, and carbon nanotubes are applied in cosmetics. Mineral-based nanoparticles containing with zinc, iron, or titanium can be applied as ultraviolet light protection. Carbon-based nanoparticles, such as carbon nanotubes, can be applied as antioxidant in cosmeceuticals. The nanocarriers is one of the nanotechnology applications that aim for transporting the safely and securely nanoscale package that contain the active compounds from one part of the host (e.g., tissue, cell, subcellular structure) to another controlled target. This process is the nanovehicles that can deliver active ingredients to a desired site in the epidermis or dermis with minimal toxicity and depth of penetration. The permeation rate of drugs can be enhanced with nanoparticulate delivery. Nanoparticles in cosmeceuticals application can be employed for photoprotection, rejuvenation (anti-aging), fragrance and drug delivery devices. Nanotechnology is the science of precise design on the nanoscale. The unique properties of matter on this scale can apply in dermatologics as
nanocosmeceuticals and nanopharmaceuticals. Using nanocarriers for active ingredient stabilization and targeted delivery, nanomaterials can be used for the restoration of skin health and the alleviation of skin disease.

iii) Agrochemicals: Nanofertilizer and fertilizer/active compound entrapment

Agrochemical is agricultural chemical that refer to pesticides, herbicides, fungicides and nematicides and also fertilizers, hormones and other chemical growth agents. Nanotechnology and nanoparticles (NPs) also play important roles in agricultural application. They possess as beneficial effects on agriculture purposes, for example TiO$_2$ NPs play beneficial roles in seed germination, enhanced root-shoot length, and improved growth of seedlings in Arabidopsis thaliana (L.) (Szymańska, et al., 2016) cabbage, corn, lettuce (Lactuca sativa L.), and oat (Avena sativa L.) (Knap et al., 2017 and Lyu et al., 2016). The sizes of NPs are so small that they can easily penetrate through the cell wall of plant roots and may cause devastating effects (Rai et al., 2015). NPs are used to improve seed germination, control fertilizer losses (nanofertilizers or nanoencapsulated nutrients), boost plant metabolism, act as a carrier for DNA and chemicals inside cells, improve genetic manipulation and expression in targeted cells, enhance photosynthesis by the introduction of carbon nanotubes (CNTs) in chloroplast that capture more light energy of higher wavelengths (UV, green, and near infrared), and improve growth and yield of crop plants. (Torney et al., 2005; de la Rosa et al., 2013; Nair et al., 2011; Labiani et al., 2013; Giraldo et al., 2014; Giraldo et al., 2014; Siddiqui and Al-Whaibi, 2014; Shweta et al., 2016)

NPs is also essentially used as carriers of herbicides, pesticides, fertilizers, and genes to target specific plant organelle. It is known that fertilizers play a role in efficient plant growth and development when it is particularly used as in a controlled release system. For the nanotechnology in agriculture application, nanofertilizers or nanoencapsulated nutrients can be applied for minimizing nutrient and increasing crop yield. The advantages of nanofertilizers are (1) reduced leaching losses of nutrients from root zone and consequently decreased environmental pollution; (2) restricted conversion of usable forms of nutrients to unusable/unwanted forms; (3) limited toxic accumulation of soluble salts in root zone, thus preventing plant damage; (4) cost reduction; and (5) enhancement of plant nutrient uptake with the characteristics of slow release of nutrients.
2. Radiation-driven nanotechnology: From simple to advanced fabrication

It is known that all irradiation techniques can be applied to fabricating and controlling diversity of nanostructures based on Top-down and Bottom-up processes. For example, degradation and grafting may be considered as Top-down process; on the other hand, polymerization, crosslinking and reduction reaction may be considered as Bottom-up process. A single irradiation technique or combined appropriate techniques provide a wide variety of nanostructures, such as metallic nanoparticles, core-shell nanoparticles, hybrid nanoparticles, nanoparticle networks, nanocomposite, nanoporous/3D nanostructure, nanogels, nanowhiskers and nanofiber (Scheme 1).

Since 2008 to present, our group have developed several types of nanoparticles using irradiation techniques, such as degradation, graft copolymerization, crosslinking and reduction as well as the combination of such techniques as classified in the following detail.

i) Polymeric nanocolloids
A simple technique of radiation-induced chain scission of natural polymers (i.e., chitosan) for systematically controlling nanoscale polymer colloids have been reported by our group (Pasanphan et al., 2010). It was found that the pre-formulation of polymer, i.e. solid, acidic solution and colloidal in aqueous solution under irradiation including the post-preparation protocol affects the particle size of the obtained colloidal products. Irradiation doses directly influence the polymer colloid size by reducing the size from 175 nm to 50 nm when gamma irradiation dose was increased from 0 to 40 kGy (dose rate = 10 kGy/h, air atmosphere). Water soluble chitosan nanoparticles (WSCS NPs) were also developed using radiation induced chain scission in aqueous acetic acid and then neutralized to obtain chitosan nanocolloids with the particle size as small as 12 nm and 50 nm (Pasanphan et al., 2015). The WSCS-NPs were prepared by simply irradiation with the dose of 80 kGy accompanying with appropriate separation. The WSCS-NPs product was well characterized to confirm it remaining chemical structure after irradiation. The changes in chain packing structure, thermal stability and morphology of the obtained WSCS-NPs reflect the improvement of its solubility, nanoscaled structure and reactivity. TEM image confirmed the successful preparation of nanometer-sized WSCS without derivatization.
WSCS-NPs exhibited more excellent antioxidant activity with the EC50 (0.115 mg/mL) than CS-HOAc (0.09 mg/mL). Compared with CS-HOAc, WSCS-NPs are non-toxic and more biocompatible to human skin fibroblasts.

In the later year, we also develop another type of biopolymeric nanocolloid, i.e., silk fibroin polypeptide. It was also found that radiation reduce the molecular weight of silk fibroin from 250 kDa to 37 kDa. (Wongkrongsak, Tangthong, Pasanphan, 2016). Although the electron beam in the dose range of 1–30 kGy induced chain scission of SF causing its MW reduction and morphological change, the main characteristic chemical structure of SF still remains. The particle size of the SF is possible reduced to as small as 40 nm when SF is electron beam irradiated with a dose of 30
kGy. The study proves that water soluble silk fibroin NPs (WSSF-NPs) show an effective-radical scavenging ability with a low EC50 of approximately 0.2 mg/mL to reduce an initial DPPH radical concentration of 150 μM by 50%.

Regarding to the previous studies, it can be summarized that radiation-induced chain scission of biopolymer can promote the production of polymer nanocolloids and enhance their properties, such as reactivity, water solubility, antioxidant and reducing activities. The radiation-induced chain scission is particularly considered as the most simple, effective and mind technique for the nanoscale-controlled synthesis of biopolymeric nanoparticles.

ii) Core-shell and functionalized polymeric nanoparticles:
Accordingly, the effect of irradiation doses on the particle sizes of the final functionalized chitosan product was also investigated (Pasanphan et al., 2012). The irradiated chitosan colloids were chemically functionalized with deoxycholic acid (DA) in order to prepare hydrophobic core structure of chitosan nanoparticles. It was found that the particle size of hydrophobic modified chitosan colloidal could be controlled and reduced by pre-irradiation. The particle size of DA-functionalized chitosan nanoparticles was mostly identical in size—approximately 30-50 nm when compared with the DA-chitosan without pre-irradiation (~125±30). The previous reports confirmed the opportunity of radiation-induced chain scission for controlling the size of polymer colloid or even its consequently functionalized product. In the next few years, radiation-induced grafting of polyethylene glycol monomethacrylate (PEGMA) on to DA-chitosan nanoparticles was established in order to prepare core-shell chitosan nanoparticles (Pasanphan et al., 2014). Grafted-polymer shell and particle size can be controlled by degree of grafting or irradiation dose. The PEGMA shell thickness and the particle size of DA-chitosan-PEGMA varied in the ranges of 10–30 nm and 70–130 nm, respectively. Based on a comparison of particle size and DG, the particle size increased from 79±12 to 116±13nm when the degree of grafting increased from 75 to 174%. An absorbed dose of 2 kGy was sufficient for grafting PEGMA onto DCCS particles to form individual core–shell PEGMA-g-DCCSNPs with an average particle size of 80 nm and PEGMA shell thickness of 10 nm. This type of core-shell nanoparticles can be applied as nanocarrier for encapsulating the active compounds, such as anticancer drug, berberine (BBR) antimicrobial substance. The PEGMA-g-DCCSNPs exhibited 30% encapsulation efficiency of BBR compound, and it was possible to control release at generally10–20% over a period of 23
days. Radiation-induced graft copolymerization method could serve as a practical and green technique for efficiently synthesizing core–shell polymeric drug carriers in a controlled release system for biomedical applications.

In the same year, poly (stearyl methacrylate) (SMA) was grafted onto chitosan colloid in order to modify chitosan surface as compatibilizer for polylactic acid (PLA) bioplastic blends. (Rattanawongwiboon, Haema and Pasanphan, 2014). Similarly, PEGMA plasticizer was grafted onto chitosan nanoparticle for PLA bioplastic blends (Kongkaorophtham et al., 2015). In addition, chitosan-SMA was functionalized with piperidine (PPD) antioxidant molecule. It was found that pre-irradiation of chitosan colloidal before grafting with poly (SMA) and functionalizing with PPD reduced the particle size of the obtained chitosan-SMA-PPD nanoparticles (Rattanawongwiboon and Pasanphan, 2014).

iii) Metallic nanoparticles:

Polysaccharide (i.e., chitosan, CS) and polypeptide (i.e., silk fibroin, SF) have been studied as biopolymer stabilizer for the synthesis of metallic NPs under irradiation-induced reduction reaction. Silver nanoparticles (AgNPs) was synthesized in CS aqueous acetic acid solution using electron beam irradiation process (Jannoo et al., 2015). It was found that AgNPs synthesis can be controlled by CS molecular weight (MW) and concentration, AgNO_3 precursor concentration, irradiation dose and tert-butanol additive concentration. Electron beam irradiation is an effective technique for preparing the AgNPs in chitosan stabilizer. The irradiation dose accompanying with all components, that is MW of CS, AgNO_3 concentration and tert-butanol are important parameter for producing of stable and high amount of AgNPs. The previous work suggested that AgNPs can be efficiently prepared using only 2.5 mM AgNO_3 in CS (MW = 580 kDa) under exposing to electron beam with a dose of 10 kGy. Most of the AgNPs synthesized under previous studied conditions are spherical shape and the averages sizes are as small as 5–20 nm. The addition of tert-butanol is not necessary when synthesizing AgNPs in CS stabilizer. Without CS stabilizer, tert-butanol can assist the synthesis of AgNPs under electron beam irradiation and 20% v/v tert-butanol is sufficient to achieve highest AgNPs amount. The AgNPs in CS stabilizer are more stable over one year when they are kept at low temperature of –5°C in the refrigerator. Regarding to the application, the electron beam synthesized AgNPs in CS stabilizer clearly exhibited antifungal capacities. The AgNPs better inhibited the growth of black and green molds than the AgNO_3. The
AgNPs showed robust antifungal effects to the *C. lunata, Trichoderma sp.*, *Penicillium sp.* and *A. niger*, respectively.

In the same year of 2015, water-soluble chitosan nanoparticle (WSCS NPs) was developed as mentioned previously (Pasanphan et al., 2015). WSCS-NPs substantially assist production of monodispersed AuNPs in one-pot reaction and mind condition. As CS is a bio-based polymer, WSCS-NPs are expected to provide a novel, practical, naturally desired water-soluble polysaccharide antioxidant in applications where safety reasons are a main concern. This simple and rapid green synthesis of AuNPs using WSCS-NPs can further be applied in biomedical areas, such as drug carrier, therapy and diagnostic applications.

In the next year, our group successful developed WSSF-NPs exhibiting superior antioxidant and reducing activities than non-irradiated SF. It was evidently found that WSSF-NPs could reduce Au (III) to Au (0), leading to gold nanocolloids formation. This novel type of the natural peptide-based nanoparticles produced from a value-added silk waste could be a natural antioxidant additive for foods, cosmetic and medical applications. In addition, its impressive reducing capacity would be a useful natural reducing agent for green synthesis of gold nano-colloids and even other metal nanoparticles for medical purpose (Wongkrongsak, Tangthong, Pasanphan, 2016).

In addition, it is very well known that radiation-induced reduction reaction be a green synthesis of metallic NPs. We also studied the green synthesis of AuNPs in water-soluble chitosan (WSCS) in comparison with the conventional CS in aqueous acetic acid (CS-HOAc) (Piroonpan and Pasanphan, 2018). In this case, the different chitosan polymer templates were used for a green synthesis of gold nanoparticles (AuNPs) under gamma irradiation. The CS-HOAc and WSCS exhibited different capacity for AuNPs formation under various irradiation doses and HAuCl₄ precursor concentrations. With the irradiation dose ~0-50 kGy, the particle sizes of the spherical AuNPs formulated in WSCTS and CTS-HOAc were in the range of 5 to 25 nm and 5 to 80 nm, respectively. The AuNPs particle size and amount can be controlled by balancing all parameters, i.e., chitosan template, HAuCl₄ concentration and absorbed doses. It has been learned that short chain WSCTS giving higher reducing efficiency (Pasanphan et al., 2015) could be an effective polymer template for AuNPs formation due to its stabilization and reducing capacities. The coordination of Au (III) on to the deprotonated WSCS in aqueous solution might affect AuNPs formation even without irradiation. The small particle size of AuNPs are limited by the number of
Au (III) atoms coordinated on the glucosamine units of short chain WSCS as already explained in the literature (Vo et al., 2014). On the other hand, Au (III) was not perfectly coordinated on to the protonated CTS-HOAc. Thus, mode of stabilization of CS-HOAc happens after nucleation and growth of AuNPs. The size of the AuNPs particle formed in CTS-HOAc should be larger than that formed in WSCTS. It can be considered that after the reduction reaction by irradiation the particle size of initial AuNPs is due to the template effect because of chitosan chain. It is also worthy to note that, the AuNPs prepared in WSCS showed lower toxicity and they also promoted cell proliferation of human skin fibroblast cells. The different CS solution systems played an important role of the template for AuNPs formation under irradiation. WSCS would be a challenging polymer template for green synthesis of AuNPs for healthcare or cosmeceutical applications.

iv) Nanogels:

Recently, we successfully develop interpolymer complex nanogel (IPC NGs) using gamma-ray irradiation (Rattanawongwiboon et al., 2018). The PAA-PEO nanogel was successfully prepared by a simple two-step technique. This has been achieved by first formation of interpolymer complexes in water and then gamma-irradiation of their solutions to induce crosslinking. The nature of solvent plays an important role in the formation of hydrogen-bonded complexes between PAA and PEO. By adding acetone in the medium, polymer-solvent interactions were weakened to facilitate IPC formation which led to the decrease of size as a result of polymer collapse. The preparation PAA-PEO IPC in 25% (v/v) acetone/water mixture was found to provide the appropriate condition for controlling size of IPC. An absorbed dose of 2 kGy was sufficient for inter- and intra-chain crosslinking to obtain PAA-PEO IPC nanogels. The permanent covalent bonding of IPC nanogels led to the stability of size and surface charge against changing temperature and pH. Dual functionality imparted by the two polymers has been considered as an advantage for applications in human body. PAA-PEO nanogels exhibited an average size of ~200 nm and maintained their stability in 25% (v/v) acetone/water mixture over a period of 2 months. The inherent properties of the polymer pairs forming the nanogels show good opportunity to be used for drug delivery system. Both polymers are approved for biomedical applications by the FDA. After the preparation of nanogels as described in this study, acetone can be easily evaporated to make the dispersion of nanogels acetone-free for the intended uses. Especially, their contraction in response to changing pH and temperature can make them suitable for controlled release.
of drugs. Hence, we will also extend our work in the future to study the performance of active compound loaded PAA-PEO IPC nanogels for healthcare and cosmeceutical applications.

The overall programme of work for the whole duration includes the development of different nanostructures mainly using irradiation techniques as show in SCHEME 2. The developed nanostructures include 1) Polymer-stabilized-metallic nanoparticles for coating/printing or cosmeceuticals, 2) Hydrophobic polymer shell modified SiO$_2$NPs for coating/printing, 3) Polymer shell-grafted-SiO$_2$ NPs for metallic NPs immobilization for coating/printing, 4) Polymeric shell-grafted-GO NPs for metallic NPs immobilization for coating/printing (conductive inks), 5) Interpolymer complex nanogels (IPC NGs) for active compound entrapment for coating/printing (high performance ink), cosmeceuticals and agrochemicals, 6) Polymer core-shell nanoparticles for active compound entrapment for cosmeceuticals and agrochemicals, 7) Interpolymer complex nanoparticles (IPC NPs) for active compound entrapment for agrochemicals and 8) Hydrogel template for nanostructure fabrication as smart agrochemicals and 2D/3D printing materials. The detailed of each development are given below.

i) Polymer-stabilized metallic nanoparticles (NPs) (Applications: Coating/printing and Cosmeceuticals)

Preparation of polymer stabilized silver nanoparticles (AgNPs), cupper nanoparticle (CuNPs) and gold nanoparticles (AuNPs) using radiation induced reduction reaction will be future studied. AgNPs and CuNPs will be mainly applied for conductive inks in coating/printing technology. For AuNPs, they will be considered as cosmeceuticals additive. Although the preparations of some metallic NPs, i.e., AgNPs and AuNPs, have been somewhat studied and published. It is still important to further study the appropriate system of stabilizing polymers particularly suitable composition for coating/printing and suitable properties as conductive inks. In this way, stabilizing polymer (e.g., polyvinyl pyrrolidone, PVP) or conductive monomer or polymer (e.g., pyrrole or polypyrrole) will be used as polymer precursor forming as stabilizer for AgNPs and AuNPs preparation using irradiation technique. For cosmeceuticals, water-soluble polymers (e.g., chitosan and silk fibroin peptide) will be also considered for AuNPs synthesis. AuNPs in water-based system and antioxidant polymers will be expected to be accelerative additive promoting human skin fibroblast proliferation in the treatment of skin, burns, wounds.

ii) Hydrophobic polymer shell modified SiO$_2$NPs (Applications: Coating/printings)
The humidity during transportation and storage is the main concern of paper packaging damage because paper readily absorbs water vapor. Superhydrophobic surface is an important issue for paper industry. Silica nanoparticles (SiO$_2$ NPs) surface was firstly modified with vinyltrimethoxysilane. Hydrophobic monomer, i.e., dodecyl methacrylate (DMA) will be grafted onto the vinyl-SiO$_2$ NPs using radiation grafting technique to obtain PDMA-g-SiO$_2$ NPs. The effect of irradiation dose and monomer concentration on degree of grafting and nanoscale-controlled grafting will be studied. PDMA-g-SiO$_2$ NPs were characterized by FT-IR, TGA, XRD, FE-SEM and TEM. The PDMA-g-SiO$_2$ NPs mixed with polylactic acid (PLA) bio-based polymer binder were coated onto paper surface using K-bar coating method. The nanostructure surface morphologies of coated paper were investigated using FE-SEM and AFM. The surface hydrophobic properties on the surface will be characterized using contact angle. The properties, such as gloss value, opacity, and color, of the PDMA-g-SiO$_2$ NPs coated paper will be also examined.

iii) Polymer shell-grafted SiO$_2$ NPs for metallic NPs immobilization (Applications: Coating/printing)

Radiation-induced surface modification of SiO$_2$ nanoparticle (NPs) was proposed for the preparation of hybrid nanostructured materials. SiO$_2$ NPs surface was modified with polymer brushes using radiation-induced grafting technique. Not only monomers containing hydrophobicity as mentioned but also monomer containing antimicrobial function, i.e., 2-(dimethylamino) ethyl methacrylate (DMAEMA) will be decorated onto vinyl modified SiO$_2$ NPs using pre-irradiation or simultaneous radiation grafting processes. The effects of monomer concentration, irradiation doses and other grafting parameters on degree of grafting were observed. Poly (2-dimethylamino) ethyl methacrylate (PDMAEMA) brushes grafted on SiO$_2$ NPs were characterized using gravimetric measurement, FT-IR, TGA, TEM and FE-SEM. The obtained SiO$_2$-g-PDMAEMA will be used as polymer shell template for silver nanoparticles (AgNPs) stabilization. In this way, AgNPs will be additionally created via radiation-induced reduction. AgNPs formation will be confirmed using UV-vis and TEM. The particle size of AgNPs immobilized on the SiO$_2$-g-PDMAEMA. Antifungal properties of the hybrid SiO$_2$-g-PDMAEMA-AgNPs will be studied.
iv) Polymeric shell-grafted-GO NPs for metallic NPs immobilization (Applications: Coating/printing)

Radiation-induced surface modification or functionalization of graphene oxide (GO) will also be included in the project in order to approach conductive inks for high performance coating/printing applications. Radiation induced grafting and radiation-induced metallic reduction will be considered to produce the reduced graphene oxide (rGO), stabilizing polymer, conductive polymer shell and metallic NPs to approach high performance conductive properties. GO surface will be modified with stabilizing polymer (e.g., polyvinyl pyrrolidone, PVP) or conductive polymer (e.g., polypyrrole) brushes using radiation-induced graft-copolymerization technique. Beside grafting, GO will be expected to reduce to graphene leading to increase its conductivity. In terms of grafting, the effects of monomer concentration, irradiation doses and other grafting parameters on degree of grafting will be investigated. The grafted polymeric shell on rGO will also be characterized using gravimetric measurement, FT-IR, TGA, TEM, FE-SEM, and AFM. In addition, the metallic NPs (e.g., AgNPs or CuNPs) will be constructed onto GO along with the grafted-stabilizing polymers using radiation induced-reduction mechanism. Formation of the metallic NPs will be confirmed using UV-vis, TEM and AFM. Conductivity of the developed materials will be observed. To approach more practical process for coating/printing, study on the simultaneous synthesis and fabrication system will be considered.

v) Interpolymer complex nanogels (IPC NGs) for active compound entrapment (Applications: Coating/printing, cosmeceuticals, agrochemicals)

Interpolymer complex nanogel have been developing using radiation-induced crosslinking techniques. Recently, poly (acrylic acid)-poly (ethylene oxide) (PAA-PEO) interpolymer complex (IPC) was prepared with equimolar stoichiometric ratio of repeating units and converted to crosslinked nanogels via γ- ray irradiation of aqueous acetone solutions. In the present work, we continuously develop PAA-PEO and other types of IPC, such as PAA and polyvinyl pyrrolidone (PAA-PVP). The effect of pH, polymer molecular weight and concentration on IPC nanogel synthesis using irradiation will be continuously studied. The hydrodynamic sizes (Rh), radius of gyration (Rg) and coil density will be determined using dynamic and static light scattering techniques (DLS and SLS). The nanostructure morphologies will also be observed using TEM, FE-TEM, FE-SEM and AFM. The thermal stability of the crosslinked IPC nanogel will be
measured TGA and DSC. The obtained PAA-PEO or PAA-PVP IPC nanogels will be applied for pigment entrapment for coating/printing applications. Moreover, the IPC nanogels will be used as polymer nanostructure template for construction of the metallic nanoparticles for high performance inks development. In addition, the synthesis of natural polymer-based IPC nanogel will also be considered for active compounds (e.g., Vitamin) entrapment and for moisture retention in the cosmeceuticals.

vi) Polymer core-shell nanoparticles for active compound entrapment (Applications: Cosmeceuticals)

Amphiphilic core-shell nanoparticles have been developing for active compound encapsulation and controlled release. Hydrophobic deoxycholic acid (DC) will be functionalized onto non-irradiated chitosan (CS) and water-soluble chitosan (WSCS) prepared from radiation-induced chain scission as mentioned. Subsequently, hydrophilic polymer shell, i.e., poly (ethylene glycol) monomethacrylate will then be grafted on to DC-CS and DC-WSCS by radiation-induced graft copolymerization technique. The effects of chitosan raw materials (CS and WSCS) radiation-absorbed dose and grafting solution on the degree of grafting and particle size of DCCS-g-PEGMA and DCWSCS-g-PEGMA will be determined. Chemical structure and change of packing structure will be determined using FTIR and XRD. Owing to their amphiphilic architecture, DCCS-g-PEGMA and DCWSCS-g-PEGMA can be self-assembled into spherical core–shell nanoparticles in aqueous media. The particle sizes were measured by TEM and DLS. Natural antifungal, i.e., berberine (BBR) and water insoluble drug will be used for studying encapsulation efficiency.

vii) Interpolymer complex nanoparticles (IPC NPs) for active compound entrapment (Applications: Agriculture)

Chitosan-poly (acrylic acid) (CS-PAA) interpolymer complex nanoparticles (IPC NPs) will be fabricated by radiation-induced copolymerization. The CS-PAA IPC nanoparticles are proposed as a nano-fertilizer by nitrogen entrapment and slow release function. The nanosized control of the CS-PAA IPC nanoparticles will be investigated regarding to different parameters, i.e., CS template with different molecular weights (CS0 = ~76 and CS80 = ~6 kDa), radiation absorbed doses and acrylic acid (AA) monomer concentration. The obtained CS-PAA IPC nanoparticles were characterized using FT-IR, XRD, TGA. Morphological studies of the CS-PAA IPC nanoparticle were verified using FE-SEM and TEM. pH responsive properties of CS-PAA
nanoparticles will be investigated in order to understand the function of controlled release of its structure. Nitrogen fertilizer will be entrapped into CS-PAA nanoparticles and controlled released of the nanoparticle will be studied. The fertilizer entrapped CS-PAA nanoparticles will be a smart agrochemical product.

viii) Hydrogel template for nanostructure fabrication (Applications: Cosmeceuticals and Agrochemicals)

Polymeric hydrogel is well known three-dimensional (3D) network material for several applications, such as wound dressing, super-water adsorbent, moisture retention and active facial mask, tissue engineering scaffold. To develop value-added hydrogel or smart hydrogels, it can be used as 3D polymer template for nanoparticle construction. Hydrophilic polymer hydrogel will be fabricated using radiation crosslinking or radiation polymerization-crosslinking techniques. In these ways, the preparation of hydrogels can be started from hydrophilic monomer or polymers or binary mixture. In addition, nanoparticles, e.g., metallic nanoparticle, polymeric or IPC nanoparticles will be constructed within the hydrogel matrix using appropriated radiation synthesis techniques. Two steps of preparation or even single simultaneous controlled-synthesis and fabrication of the nanostructure in hydrogel structure will be designed. For example, CS-PAA IPC nanoparticle (as in C.7) will be constructed in the super-water adsorbent hydrogel to achieve smart agrochemical materials by moisture retention and fertilizer-controlled release due to pH responsive function of CS and PAA. An additional example is AuNPs nanoparticle constructed in biopolymer hydrogels as an active facial mask for cosmeceutical applications.

The overall programme of work for the whole duration includes the development of different types of nanostructured materials using irradiation techniques and their opportunities to be used in different purposes is summarized in the following table. The stages of development of each nanostructure are different depending on the background of previous work and the future opportunity of the new types of nanostructures for higher performance materials and new value-added products using radiation-controlled processes.

In summary, the overall programme of work for the whole duration includes synthesis, fabrication and characterization of the studied nanostructure prepared by radiation-induced chemical reaction and processing is presented in Table 1. The expected output of the project under this CRP are provided in Table 2.
TABLE 1. OVERALL PROGRAMME OF WORK FOR THE WHOLE DURATION OF THE CONTRACT

<table>
<thead>
<tr>
<th>Programme of work</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Polymer-stablized-metallic nanoparticles</td>
<td>1</td>
</tr>
<tr>
<td>2) Supperhydrophobic polymer shell modified SiO2NPs</td>
<td>2</td>
</tr>
<tr>
<td>3) Polymer shell-grafted-SiO2 NPs for metallic NPs immobilization</td>
<td>3</td>
</tr>
<tr>
<td>4) Polymeric shell-grafted-GO NPs for metallic NPs immobilization</td>
<td>4</td>
</tr>
<tr>
<td>5) Interpolymer complex nanogels (IPC NGs)</td>
<td></td>
</tr>
<tr>
<td>6) Polymer core-shell nanoparticles for active compound entrapment</td>
<td></td>
</tr>
<tr>
<td>7) Interpolymer complex nanoparticles (IPC NPs) for active compound entrapment</td>
<td></td>
</tr>
<tr>
<td>8) Hydrogel template for nanostructure fabrication</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2. EXPECTED OUTPUTS OF THE PROJECT

<table>
<thead>
<tr>
<th>Outputs</th>
<th>Indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Product prototype:</td>
<td>At least 1 submitted national patent/petty patent by the end of CRP.</td>
</tr>
<tr>
<td>2. Techniques and processes:</td>
<td>At least 4 ISI publications by the end of CRP.</td>
</tr>
<tr>
<td>3. Network with industry (or end-user)</td>
<td>At least 1 national industrial-linked project supported by national</td>
</tr>
<tr>
<td>4. Network of collaboration in this field:</td>
<td>At least 2-3 international collaborations established or developed during the CRP</td>
</tr>
</tbody>
</table>
REFERENCES:


TURKEY

FORMATION OF PALLADIUM NANOCLUSTERS VIA RADIATION-INDUCED REDUCTION OF PALLADIUM IONS ABSORBED ON POLY(VINYLPYRROLIDONE) SHELL GRAFTED ON SILICA MICROPARTICLES BY RAFT POLYMERIZATION AND INVESTIGATION OF THEIR CATALYTIC ACTIVITIES

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Abstract

Surface functionalization of inorganic materials with a polymer shell is attracting attention because the polymer coating alters the interfacial properties of the modified particles. In this work, we have synthesized a silica based macro initiator by attaching azo-initiator to silica particle surfaces and then used it to polymerize vinyl pyrrolidone (VP) via Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization method. The effects of varying monomer and RAFT agent concentrations along with polymerization time have been examined. The resulting PVP modified silica particles were characterized by various methods. The synthesized particles are attractive due to their well-defined structures and the ease of synthesis. The PVP-grafted silica surface was then used to absorb Pd(II) ions in aqueous solution. Pd (II) absorbed particles were irradiated by gamma-rays to reduce the metal ions into nanoparticles as metallic clusters. Palladium (Pd) is an important member of noble metals that has long been used as a catalyst. Pd catalysts are important as they particularly enable to control the selectivity in semi-hydrogenation of various compounds. PVP was specifically preferred as a protecting polymer shell due to its effectiveness in protecting metallic nanoparticles against oxidation and aggregation. It is expected that the synthesized particles will be attractive as a heterogeneous supported catalyst due to their well-defined structures and ease of synthesis. Investigation the catalytic effects of the particles synthesized will be the future works of our on-going study.
1. INTRODUCTION

Over the past few decades, the progress in synthesis of new materials in the nanosize region resulted in revolutionary developments in science and engineering as these materials present unique properties that are significantly different from those of their bulk counterparts. Metal nanoparticles are one of the most versatile and promising ones among the nano-sized materials and can be used in many applications such as catalysts, medicine, microelectronics, etc. [1].

Metal colloids are generally prepared via the reduction of precursor metal ions in solution in the presence of a stabilizing agent. Irradiation, using of chemical reducing agents and thermolysis are among the most commonly used techniques [2]. High reproducibility and mild reaction conditions such as ambient temperature and pressure are the among biggest advantages of radiolytic synthesis compared to other available methods [3]. Furthermore, the hydrated electron which is the main reducing agent formed in the absence of oxygen enables any metal ions to be reduced to zero-valent metal atoms without using chemical reducing agents. Under irradiation, the production of primary atoms occurs independently and homogeneously as each ionic precursor is distributed uniformly and reduced individually. This along with the elimination of excess chemical reducing agents lead to the formation of highly stable and homogeneously dispersed nanoparticles. Absorbed radiation dose is very effective in controlling the cluster size and crystal structure. by precise tuning of nucleation and growth steps especially for multi-metallic clusters. Therefore, radiolytic synthesis of metallic nanoclusters has been attributed as an environmentally benign and low-cost method for controlling the size and structure of metal nanoparticles by precise tuning of nucleation and growth steps [5, 6].

Palladium (Pd) is a prominent member of noble metals used as catalysts. Pd catalysts are regarded as extremely versatile tools in organic chemical synthesis as they able to fine-tune the reaction conditions such as solvents, ligands, temperature, etc. Cross coupling and related reactions, such as direct arylation, the Buchwald-Hartwig the Heck reactions are among the most versatile and useful tools for the realization of organic synthesis in both academic and industrial terms [7]. In general, all these reactions require a transition metal catalyst to proceed at a synthetically beneficial rate. Although capable of other metals are able to catalyze various stages of these reactions, Pd-
based catalysts dominate the synthetic applications. Furthermore, these reactions are generally regarded as standard methods for evaluating the reactivity of Pd species as potential catalysts [8].

Despite the promising features of Pd nanoclusters, they are unstable in a solution and agglomerate in bulk. To enhance the stability of Pd NPs, polymeric support materials are mostly needed. Poly(vinylpyrrolidone) (PVP) has reportedly the highest stabilizing effect on many metallic NPs in comparison with other widely used stabilizers such as poly(acrylic acid) or poly(N-vinylimidazole) [9]. In our work we, therefore, chose PVP as polymeric stabilizing matrix. A thin PVP layer was grafted on the silica microparticle surface as explained in detail below. The grafting was carried out via RAFT polymerization method as it provides control over the molecular weight and architecture of the grafted PVP chains. The catalytic properties of metal NPs are generally regarded as size- and shape-dependent [10]. However, the characteristics of the stabilizing matrix on which the NPs adsorbed also play a crucial role in their catalytic properties [11, 12]. Therefore, establishment of a method yielding tailor-made and well-defined characteristics over the stabilizing matrix is one of the key points to attain monosized NPs with homogeneous distribution and reproducible catalytic activity. This target will be achieved by applying RAFT polymerization during the formation of PVP shell. This polymerization method is regarded as the most versatile and effective mechanism among the other controlled polymerization methods in tailoring the characteristics of the polymer chains. We have an undeniable experience in the field of surface modification of various substrates via radiation-induced RAFT mediated graft copolymerization method [13-18].

In the present study, a thin PVP shell was formed on silica microparticles via RAFT mediated graft copolymerization method. The resultant core-shell particles with silica at the core and PVP as the shell were later be used for stabilizing Pd NPs formed under irradiation. Grafting of PVP on silica is preferred over soluble PVP chains in solution, because it provides a facile isolation of PVP-stabilized Pd NPs from the reaction medium. In future works, silica-supported and PVP-stabilized Pd NPs will be tested for their catalytic effects on well-known model catalytic reactions. The Suzuki reaction is a widely used coupling reaction to synthesize substituted biphenyls, styrenes and poly-olefins, where the coupling partners are a boronic acid and an organohalide catalyzed by a palladium (0) catalyst [19, 20]. This reaction is widely regarded as a standard method to evaluate the reactivity of Pd species as potential catalysts. Therefore, we plan to perform Suzuki coupling reaction in the proposed project to compare the results attained with those in literature.
It was first published by Akira Suzuki in 1979 and shared the Nobel Prize in Chemistry in 2010. In many publications, this reaction is also referred to as the Suzuki-Miyaura reaction and is also called Suzuki mapping. Poly-olefins are commonly used to synthesize styrenes and substituted biphenyls [19, 20]. The Suzuki reaction is an organic reaction classified as a coupling reaction in which the coupling partners are a palladium (0) catalyst and a catalyzed by a boronic acid and.

First published in 1979 by Akira Suzuki and shared the 2010 Nobel Prize for Chemistry. In many publications, this reaction is also called Suzuki-Miyaura reaction and is also called Suzuki kuplaji. Poly-olefins, styrene and replaced biphenyls [19, 20] are widely used for synthesis.

A high catalytic activity is desirable for academic and industrial applications. The catalytic properties of metal NPs are generally regarded as size- and shape-dependent [21]. However, it is a fact that the characteristics of the stabilizing matrix on which the NPs adsorbed also play a crucial role in their catalytic properties [22, 23]. Therefore, establishment of a method yielding tailor-made and well-defined characteristics over the stabilizing matrix is one of the key factors to attain monosized NPs with homogeneous distribution and reproducible catalytic activity. It is reported that the mean diameter of Pd nanoparticles increases with increasing molecular weight of the stabilizing polymer soluble in solution medium [24]. Shimmin et al., on the other hand, reported that particle size decreases with increasing polymer molecular weight due to polymer’s steric bulk in blocking particle growth, yielding more small particles rather than fewer large ones [25]. These two studies, which contradict with one another, examine the relation between molecular weight of the soluble stabilizing polymer in solution and nanoparticle size. To the best of our knowledge, no systematic study has been published on the relationship between the thickness of the polymer shell grafted to a substrate and nanoparticle diameter. In the proposed project, we will vary the thickness of the PVP layer on silica by tailoring the molecular weight of the grafted chains via RAFT polymerization mechanism to investigate systematically the relation between polymer shell thickness and nanoparticle size under irradiation. Along with this scope, the effects of absorbed radiation dose and dose rate on the catalytic activity of Pd NPs will be examined.

2. EXPERIMENTAL
2.1. Materials. 3-Aminopropyl-functionalized silica gel (particle size 40-63 μm, 1 mmol.g⁻¹ amino groups) with a specific surface area of 550 m².g⁻¹ was obtained from Sigma-Aldrich. 4,4’-Azobis(4-pentanoic acid) ACPA has been used as a radical initiator in polymer synthesis and was supplied from Aldrich. O-ethyl-S-(1-methoxycarbonyl) ethyl dithiocarbonate was used as RAFT agent and prepared according to literature. All other chemicals were supplied from Sigma-Aldrich.

2.2. Synthesis of 4,4’-Azobis(4-cyanopentanoic acid) (ACPA) functionalized silica (Si-ACPA)

1 g of ACPA and 0.8 g of DCC (N,N’ dicyclohexylcarbodiimide) as an activator in 50 mL of DMF were added small portions to a suspension of 2 g of silica in 20 mL DMF under vigorous stirring. The reaction mixture was stirred in the dark at 0 °C for 48 hours. The final product was filtered, cleaned and dried under vacuum at room temperature. The initiator modified silica particles were kept in the dark at 0 °C.

![FIG 1. Schematic Representation of the Synthesis of the Azo Initiator Modified Aminopropyl Silica microparticles (Si-ACPA)](image)

2.3. Synthesis of Poly(vinylpyrrolidone) (PVP) grafted silica microparticles (Si-PVP)

Polymerization solutions containing various amounts of VP and RAFT agent were subjected to thermally initiated graft-copolymerization using 0.1 g of initiator-immobilized silica (Si-ACPA) microparticles during a range of polymerization times at 65 °C and under N₂ atmosphere. PVP grafted silica particle (Si-PVP) were filtered and purified by deionized water. Then, the precipitated homopolymer (PVP) was collected by centrifugation. Finally, the separated polymers were dried under vacuum at 50 °C 12 h. A
3. RESULTS AND DISCUSSION

Pd NPs are unstable in a solution and agglomerate in bulk. To enhance the stability of Pd NPs, polymeric stabilizing materials are most widely used. In addition to be a good absorbent for many metal ions, poly(vinylpyrrolidone) (PVP) is reportedly effective in protecting nanoparticles against oxidation, aggregation, etc. PVP has reportedly the highest stabilizing effect on many metal NPs in comparison with other widely used stabilizers such as poly(acrylic acid) or poly(N-vinylimidazole) [26]. In the proposed project, a thin PVP shell will be formed on silica microparticles via reversible addition–fragmentation chain-transfer (RAFT) mediated graft copolymerization method. The resultant core-shell particles with silica at the core and a thin PVP layer as the shell, will later be used for stabilizing Pd NPs formed under irradiation. Grafting of PVP on silica, rather than using it in homopolymer form, is crucial in order to provide a facile isolation of PVP-stabilized Pd NPs from both the radiation-induced reaction solution and catalytic reaction medium. Silica-supported and PVP-stabilized Pd NPs will be tested for their catalytic activity on well-defined model coupling reactions. The reason of applying RAFT-mediated polymerization during the grafting of PVP shell is because RAFT mechanism provides a nano-scale control over the growing of grafted chains [27]. By RAFT method, it is possible to form a thin PVP layer on silica particle in a controlled and uniform manner.

In order to characterize the grafted PVP shell we used FTIR analysis as given in Fig. 2. As can be seen form this figure, grafting of PVP to silica structure significantly led to appearance of C=O peak at around 1620 cm$^{-1}$. Moreover, the absorption peak around 3500 cm$^{-1}$ can be ascribed to the CN group of PVP. The intensities of both peaks increase with increasing polymerization time, indicating an increase in grafting degree of PVP.
In order to investigate the morphological changes appeared due to surface coverage of silica by PVP layer, we have performed SEM analysis as presented in Fig. 3. As can be seen in this figure, the surfaces in (b) and (c) look free from any spurious matter such as aggregated PVP domains. This indicates that a homogeneous surface coverage took place during the grafting of PVP from silica surface.

**FIG 3. SEM images of (a) –ACPA functionalized, (b) and (c) PVP grafted silica particles.**
Palladium (II) salts are generally selected as starting species due to their high stability. In order to produce palladium (0) species entering the catalytic cycle, radiation-induced reduction of Pd ions to metallic Pd (0) is a key process due to the above-mentioned advantages of radiolytic synthesis [8]. In order to characterize the Pd(0) metallic nanoclusters formed under gamma-irradiation, we have performed TEM analysis. As can be seen in Fig.4, surface of silica is covered by a thin PVP layer and Pd(0) nanoparticles are uniformly distributed among the PVP shell.

**FIG. 4. Formation of Pd(0) nanoclusters on PVP layer grafted form silica surface.**

4. CONCLUSION

In the present study, a thin PVP shell with well-defined properties was formed on silica microparticles via RAFT mediated graft copolymerization method. The resultant core-shell particles with silica at the core and PVP as the shell were used for stabilizing Pd NPs formed under irradiation. The grafting of PVP layer and formation of Pd nanoclusters were clearly indicated by various experimental techniques. In the future studies of the proposed project, we will vary the thickness of the PVP layer on silica by tailoring the molecular weight of the grafted chains via RAFT polymerization mechanism to investigate systematically the relation between polymer shell thickness and nanoparticle size under irradiation. Along with this scope, the catalytic efficiency of the particles synthesized will be the investigated. Furthermore, the effects of absorbed radiation dose and dose rate on the catalytic activity of Pd NPs will be examined.
REFERENCES


UNITED KINGDOM

INVESTIGATION INTO RADIATION CHEMICAL SYNTHESIS OF NOBLE METAL NANOPARTICLES ON CARBON SUPPORTS FOR APPLICATIONS IN ELECTROCATALYSIS

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Abstract

This project involves the development of a new platform for controlled synthesis of carbon-supported noble metal nanoparticles, for electrocatalysis applications. More specifically, we will radiolytically synthesise a series of palladium nanoparticles on two different graphene-based supports and in four different solvents using a variety of radiation sources (gamma and X-rays, electron and particle beams). This approach will allow for a systematic investigation into the factors controlling the morphology and chemical composition of produced nanomaterials. In particular, this work will endeavor to close the gap in understanding of the effect of complexation between precursor metal ions and graphene-based templates on the relevant properties of synthesised nanocomposites. Furthermore, the project will explore whether the radiation chemistry of a solvent, deployed for the reduction reaction, can be used to effectively manipulate the shape and size-dependent properties of the metal-decorated nanomaterials. The catalytic efficiency of the synthesised nanocomposites will be screened by performing the electrooxidation of glucose into gluconic acid in alkaline conditions as well as in hydrogen evolution reaction (HER). Prepared nanocatalysts will be fully characterised in terms of their size, structure and composition. Such elaborate analysis will allow us to gain a better understanding of observed “structure-property” relationships, thus creating the scientific basis for a controlled design of nanomaterials using radiation chemical approach. The proposed work deals with several key challenges facing global economy, related, in particular, to the development of a sustainable energy model by (1) designing new rational strategies for the manufacturing of novel advanced nanomaterials and (2) promoting radiation chemical method as an alternative synthetic technique in nanotechnology. The proposed research is placed well within the remit of the IAEA’s 22070 CRP "Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology".

Project Description

Continuous progress in nanotechnology relies on the development of novel methods to synthesise nanomaterials. The main benefit expected from innovations in this field is the ability to manipulate
preparatory conditions in such a way so that the novel structure-property relationships for nanomaterials could be formed and exploited in fully predictable and reproducible manner. It is proposed here that the development of mechanistic understanding of the radiation chemical method will offer an effective alternative to the traditional techniques for the synthesis of carbon-supported metal nanoparticles.

The novelty of this research project will be in systematic exploration of the relationship between several crucial experimental parameters and the structure and properties of produced nanostructures. The experimental variables to be explored in this work are: (1) the form of graphene support precursor (liquid phase exfoliated graphene vs. dispersed graphene oxide) and (2) the chemical nature of selected solvent (radiation stable vs. easily degradable); (3) quality of radiation (X rays, gamma rays, electron and ion beams). By correlating the effect of selected experimental parameters on the properties of supported noble metal nanoparticles, the scientific basis for a rational design of these nanocomposites will be established.

The research programme will be realised by pursuing the following three objectives:

(1) radiation chemical synthesis of Pd nanoparticles on two different graphene-based supports in four selected solvents; (2) evaluation of electrochemical catalytic performance of prepared metal nanocomposites; (3) correlation of the nanocomposite properties with the type of radiation, the choice of solvent and the type of carbon substrate to develop the fundamental understanding of the reaction mechanism.

Due to the interdisciplinary character of proposed research it is expected that it will strongly impact on at least three fields: (1) radiation chemistry; (2) graphene and transition metal nanotechnology; (3) catalysis and energy conversion.

The radiation chemistry research community will benefit from the fundamental knowledge gained from the reactions of graphene templates and metal ion precursors with reducing radical species generated in selected solvents under radiolysis. Since our project departs from conventional methods for preparation of nanostructures, nanotechnology community will benefit from the development of an effective alternative fabrication technique. Finally, this research holds a great potential to enable large scale production of efficient electrocatalysts with potential use in, for example, fuel cells.
**Economic Benefits**

This proposal describes novel and ambitious research programme aiming to develop a mechanistic understanding underpinning the effective synthesis of supported metal nanoparticles using ionising radiation. Potential industrial beneficiaries of the proposed project are existing or emerging companies involved in manufacturing of advanced materials, in particular, of supported metal nanoparticles with useful functional properties. The proposed project will help to develop an industrial process that offers improved control over the properties of produced nanocomposites. In other words, the outcome of this research will benefit those manufacturers who are seeking innovative, more efficient ways to produce supported nanomaterials. By manufacturing nanoscale materials in a controllable manner with an emphasis on scalability, improved particle size distribution and environmental safety, this project is expected to benefit the industrial technology directly through creation of new products with higher added value and improved global competitiveness.

**Anticipated Outcomes**

1. Disseminating research findings through high quality journal publications and international conferences in graphene, metal nanoparticle catalysis and radiation technology areas;
2. Broadening the scope of research as well as building research capacity by developing new links and establishing strong collaborative network between the participating researchers; in particular, through the membership in this CRP;
3. Engaging with potential industrial partners and exploring commercialisation opportunities for produced “know-how”;
4. Providing unique training opportunities for career development the postdoc, who will be conducting interdisciplinary research at the interface of radiation chemistry and material science.

**Scientific Case**

The extent of radiation-induced decomposition varies significantly from one compound to another. Radiation chemists use the G-value (radiation-chemical yield, expressed in moles per Joule) as a
measure of susceptibility of a chemical system to radiation. In dilute solutions (\(\leq 0.1 \text{ M}\)), radiolysis of the solvent dominates the radiation chemistry of the system. Thereby the formation of reactive species from the solvent will induce environmental changes that will have a potential to trigger and control the growth of the nascent NPs [1]. In most irradiated solvents, the concentration of radicals reaches steady state on millisecond time scale and at that time can be characterised by the “escape” G-values. For example, gamma radiolysis of water after 100 ns can be adequately described by equation (1); the respective product G-values are given in brackets [1]:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow e_{\text{aq}}^- \ (0.28 \ \mu\text{mol J}^{-1}), \ \cdot\text{OH} \ (0.28 \ \mu\text{mol J}^{-1}), \ \cdot\text{H} \ (0.06 \ \mu\text{mol J}^{-1}), \\
\text{H}_2 & \ (0.047 \ \mu\text{mol J}^{-1}), \ \cdot\text{H}_2\text{O}_2 \ (0.073 \ \mu\text{mol J}^{-1}), \ \cdot\text{H}_3\text{O}^+ \ (0.28 \ \mu\text{mol J}^{-1})
\end{align*}
\]  

(1)

Among these water radiolysis products, the radical species, namely the hydroxyl radical \(\cdot\text{OH}\), the hydrated electron \(e_{\text{aq}}^-\) and the hydrogen atom \(\cdot\text{H}\) are the most relevant in the context of our study. Both \(e_{\text{aq}}^-\) and \(\cdot\text{H}\) are highly reactive and possess negative reduction potentials (-2.3 \(V_{\text{NHE}}\) for the hydrogen atom and -2.87 \(V_{\text{NHE}}\) for the hydrated electron). Both species are capable of reducing metal ions (\(M^{x+}\)) to zero-valence atoms (\(M^0\)) as shown by equations (2) and (3) below:

\[
\begin{align*}
M^{x+} + x(e_{\text{aq}}^-) & \rightarrow M^0 \\
M^{x+} + x(\cdot\text{H}) & \rightarrow M^0 + x(H^+)
\end{align*}
\]  

(2) \hspace{1cm} (3)

The \(\cdot\text{OH}\) is a highly oxidative radical (an oxidation potential equals to +2.73 \(V_{\text{NHE}}\)). It can readily oxidise the ions and metal atoms to higher oxidation states. Such oxidation is an undesirable process. However, the oxidation can be fully prevented by adding the \(\cdot\text{OH}\) scavengers, e.g., isopropanol, to water, cf. equation (4) below:

\[
\text{H}_3\text{C}-\text{CH(OH)}-\text{CH}_3 + \cdot\text{OH} \rightarrow \text{H}_3\text{C}-\text{C}^-\text{H(OH)}-\text{CH}_3 + \text{H}_2\text{O}
\]  

(4)
The radical H\textsubscript{3}C-C\textsubscript{2}-(OH)-CH\textsubscript{3} has reducing properties (-1.39 V\textsubscript{NHE}) and will also contribute to the reduction of metal ions (M\textsuperscript{x+}). Hence, the presence of the hydroxyl radical scavenger creates an environment suitable for a prompt reduction of metal ions into zero-valent NPs.

**FIG 1** describes the mechanism of the radiolytic synthesis of supported metal nanoparticles in an aqueous solution [2]. During the stage 1, in the presence of the \cdotOH scavengers a pool of reducing radicals is formed in the radiolysis of water. At the following step (stage 2), these species reduce the metal ions to the corresponding metal atoms M\textsuperscript{0}. Prompt reduction (stage 2) creates appreciable concentration of zero-valence state atoms M\textsuperscript{0}, which start to dimerise and further coalesce into larger metal nanoclusters (stage 3). If reaction is conducted in the presence of dispersed supporting material, e.g. graphene oxide, then the formation of nucleation centres and subsequent growth of NPs is expected to occur on the surface of this template (stages 4&5).

Importantly, the nature of reducing species formed in stage 1 depends on the solvent undergoing radiolysis. Hence, by changing the solvent a critical step of metal ion reduction can be directly controlled, as different radicals will reduce M\textsuperscript{x+} with different efficiency. Secondly, stage 2 (the reduction step) depends on the steady state concentration of reducing species. The concentration of radicals is linked directly to the G-value of radiolyzed solvent. If a solvent produces radicals in high yields, e.g. water, then the reducing species are supplied in high steady state concentration. In this case, the reduction step (M\textsuperscript{x+} → M\textsuperscript{0}) is completed on the short-time scale by formation of a large number of reduced metal atoms which subsequently become aggregation centres for the growing metal NP clusters. Hence, a large number of small size metal NPs is expected to be formed in this case. On contrary, a solvent with higher radiation stability than water, e.g. aniline, will generate low steady state concentrations of reducing radicals. Hence, the pool of metal ion
precursors will undergo the reduction into metal atoms at much slower rate. The net result of the growth mechanism in this case is likely to be the formation of a relatively small number of reduced metal centres which will subsequently grow into the NP clusters of rather large size. Thus, we suggest that by varying the solvent composition the steady state concentration of reducing agents can be efficiently manipulated, which is expected to directly impact on the size, composition and architecture of produced supported NPs.

In this study, four different solvents have been selected to provide a wide representation of liquids whose radiolysis is expected to yield different types of reducing radicals that are produced in a broad range of yields. Notably, all four solvents are well suited for exfoliation of graphene from graphite as well as for preparation of GO dispersions [3,4]. Table 1 compares the expected yields of reducing radicals to be formed in the gamma radiolysis of these solvents.

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<tr>
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<tbody>
<tr>
<td>G-value</td>
<td>1.7×10⁻⁸</td>
<td>2.0×10⁻⁷</td>
<td>7.0×10⁻⁷</td>
<td>7.5×10⁻⁷</td>
</tr>
<tr>
<td>(mol J⁻¹)</td>
<td>(low rate)</td>
<td>(intermediate rate)</td>
<td>(high rate)</td>
<td>(high rate)</td>
</tr>
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TABLE 1 RADIATION CHEMICAL YIELDS OF REDUCING RADICAL SPECIES PRODUCED IN GAMMA RADIOLYSIS OF ANILINE, N-METHYL-2-PYRROLIDONE, WATER MIXED WITH ISOPROpanol, AND ETHYLENE GLYCOL, (MOL J⁻¹).
Furthermore, the formation of metal nucleation centres and the growth of metal nanoclusters (stage 4 on FIG. 1) is likely to be affected by specific interactions of the metal ions with the supporting material. As schematically shown on FIG. 2, in contrast to graphene, graphene oxide might retain larger amounts of the metal ions due to electrostatic interactions between the oxygen-containing functional groups on the surface of GO and metal cations in solution [8]. Even though reducing radicals from the gamma radiolysis of solvents will eventually reduce GO to the reduced graphene oxide (rGO), using GO as a starting material instead of graphene is suggested to produce nanocomposites with higher content of a noble metal and greater stability of metal NP decoration. In contrast, deploying exfoliated graphene as a template is expected to result in more random distribution of somewhat larger metal nanoclusters across graphene’s surface.

Programme and Methodology
FIG. 3 presents a general overview of the methodology on which this project will rely. More specifically, the research activities will proceed through six essential steps: (1) preparation of a dispersed reaction mixture containing a selected solvent, graphene template and metal ions via ultra-sonication; (2) radiolytic synthesis of the supported metal NPs; (3&4) fabrication of electrocatalysts and screening of their efficiency by performing cyclic voltammetry analysis of the oxidation of glucose into gluconic acid and hydrogen evolution as model reactions; (5) exhaustive characterisation of the size, structure and composition of the prepared nanocomposites; (6) elucidation of the “structure-property” relationships by correlating the data from the steps 4 and 5.

REFERENCES


VIET NAM

PREPARATION OF SILVER NANO/DIATOMITE NANOCOMPOSITE BY ELECTRON BEAM IRRADIATION METHOD AND ITS CHARACTERIZATIONS

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Abstract
Electron beam (EB) irradiation of suspension mixture of AgNO$_3$/chitosan/diatomite (DA) to synthesise silver nanoparticles (AgNPs)/DA nanocomposite was investigated. The Ag$^+$/ ions of 10 mM AgNO$_3$ precursor were reduced to Ag$^0$ atoms and aggregated on DA forming AgNPs/DA nanocomposite. The AgNPs were spherical with diameter about 9 nm obtained by EB irradiation at absorbed dose of 20.2 kGy. Nanocomposites of AgNPs/DA were characterized by UV-Vis spectra with a maximal peak at around 417-422 nm. Energy dispersive X-ray (EDX) spectra for DA and AgNPs/DA nanocomposites confirmed the presence of elemental compounds in DA and atomic Ag. The antibacterial activity of the AgNPs/diatomite against E.coli as well as infectious pathogen for Tra catfish (Pangasianodon hypophthalmus) such as Aeromonas hydrophila (A. Hydrophila) was evaluated.
1. INTRODUCTION

Recently, nanoparticles and nanocomposites have been potentially applied in various fields such as nanodevices, biomedicine, cosmetic, filter aid in food, photocatalysis and antibacterial treatment in environment [1, 2]. Furthermore, new properties have been achieved through improvements in physical, chemical interactions and biological effects [3]. The development of advanced nanomaterials by combination of macromolecules with inorganic particles has become one of the most innovative research areas [4]. These nanomaterials display featured characterizations by synergistic effects resulting from interactions between inorganic nanoparticles and organic components [5]. Because of their effective antimicrobial properties and low toxicity toward animal cells, silver nanoparticles (AgNPs) have become one of the most commonly used nanomaterials in consumer products [6]. Especially, AgNPs-decorated porous silica such as ceramic, montmorillonite, zeolite, diatomite… have been used in purpose of water purification such as bactericide, antifouling agent, catalyst and decontaminant… [7]. Nanocomposite contains AgNPs which have a broad spectrum of antimicrobial activities including multi-drug resistant bacteria was studied [8, 9]. At present, AgNPs were considered as a “green” decontaminant against the bacteria in the aquatic environment such as Lactococcus garvieae, Streptococcus iniae… which were isolated from diseased rainbow trout in culture ponds [10]. The size and the morphology of metal nanoparticles as AgNPs were stabilized by chitosan, an antibacterial polysaccharide, will be suitable for purpose using nanoparticles as bactericide [11]. Preparation of nanocomposite as AgNPs/chitosan and AgNPs/silica in ceramic, diatomite or zeolite for controlling infectious agents in the environment has been necessary to substitution for the use of toxic chemicals [12]. There have been several attempts for the synthesis of nanocomposite that can be classified under two major categories: as physical and chemical methods [13]. Generally, the nanoparticle-doped material has advantages such as high performance, low price, high chemical durability, as well as avoiding aggregation of nanoparticles as AgNPs and low release metal ions as Ag⁺ for a long period of time [14]. Irradiation by electron beam (EB) or γ-rays was also reported to be effective and attractive method to prepare nanocomposite [15]. The advantage of radiolytic reduction method, over the other method, is possibility to obtain a homogeneous distribution of synthesized nanoparticles within polymer matrix as well as to control their size by changing the experimental conditions [16]. The obtained
material is high purity and sterilized at the same time which is important to use nanocomposite as a decontaminant.

In this study, AgNPs were immobilized on the diatomite by in situ synthesis. Silver ions were reduced to silver atoms by electron beam (EB) irradiation and simultaneously deposited on the diatomite. The antibacterial activity of AgNPs/DA nanocomposite against *E. coli* and *A. hydrophila* was also investigated.

## 2. MATERIALS AND METHOD

### 2.1. MATERIALS

Diatomite was purchased from Phu Yen Province, Vietnam with over 63% SiO$_2$, particle size about 10-100 µm. Chitosan with a degree of deacetylation about 80% and Mw = 1.06 × 10$^5$ was prepared as reported previously [17]. All other chemicals, including silver nitrate (AgNO$_3$), (S)-lactic acid (90%), sodium hydroxide (NaOH) were of reagent grade. Distilled water was used in all experiments.

### 2.2. PREPARATION OF AgNPs/DA NANOCOMPOSITE BY EB RADIOLYTIC REDUCTION METHOD

The diatomite (DA) samples were immersed in hydrochloric acid 3% (v/v) at room temperature for 1 hour for demineralization and washed with distilled water. Then samples were dried in an oven at 110°C. Next, 10 g DA was dispersed in 50 ml of 10 mM AgNO$_3$ in 1% chitosan solution. The suspension containing AgNO$_3$/chitosan/DA was stirred vigorously and was irradiated in air under an electron beam of UELR-10-15S2 linear accelerator (Russia), 10 MeV energy with beam current of 1.5 mA at absorbed doses of 6.5, 13.4, 20.2 and 25.9 kGy (dose rate of 5 kGy/s) measured by the Radiochromic film dosimeter (ASTM International, 2004). After that, the resultant AgNPs/chitosan/DA powders were rinsed with distilled water and then dried at 80°C for further experiments.

### 2.3. PHYSIO-CHEMICAL CHARACTERISTICS OF AgNPs/DA NANOCOMPOSITE

The UV-vis spectra of the AgNPs which were separated from irradiated AgNO$_3$/DA suspension were recorded on a Jasco V-630 spectrophotometer in the range from 200-600 nm after the solution was diluted 20 times with distilled water. EDX spectra were carried out on a SEM-EDX instrument.
– SEM S4800 (Hitachi) combined with a H7593 (Horiba) X-ray analyzer. Transmission electron microscopy (TEM) images were performed with a JEOL, JEM-1400 electron microscope at an accelerated voltage of 100 kV. The content of silver nano in AgNPs/diatomite composite was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4. ANTIBACTERIAL EFFICACY OF AgNPs/DA NANOCOMPOSITE

The antibacterial activity of the prepared AgNPs/DA sample against *E. coli* (ATCC 6538) was evaluated using spread-plate method on LB agar Petri plate with some modifications [18]. The tested bacterial suspension was prepared with $1 \times 10^8$ CFU/ml (CFU: colony forming units) of *E. coli* and added to 99 ml LB medium in each conical flask. Then 1 gram of AgNPs/DA nanocomposite was introduced into aqueous suspension of bacteria with the content of AgNPs about 13 mg/L. Flasks were shaken vigorously for 30 min, serial dilutions were made. From each of three suitable dilutions, 0.1 ml liquid was spread on LB agar plates, then incubated at 37°C for 24 h. Percent reduction of bacteria was evaluated by calculating the number of bacterial colonies on agar plates of sterilized water (control) and AgNPs/diatomite.

The AgNPs/DA nanocomposite against infectious pathogen for Tra catfish, namely *Aeromonas hydrophila* was also tested. These bacteria were cultured on BA (Blood Agar) medium, then adjusted the bacterial suspension as 0.5 McFarland standard at $10^8$ (CFU/ml) and diluted to 10$^3$-10$^4$ (CFU/ml). Next, AgNPs/DA nanocomposite was introduced in bacterial suspension with ratio of 0.2 g nanocomposite/10 ml bacterial suspension, then mixture was shaken and incubated for 3 and 24 hours. After interaction between bacteria and AgNPs in nanocomposite, 0.1 ml liquid was spread on Brain Heart Infusion Agar (BHIA) plates, then incubated at 30°C for 24 h. Percent reduction of bacteria was evaluated by the counts of survival colonies on agar plates of sterilized water (control) and experimental samples at 0, 3 and 24 hours, respectively.

3. RESULTS AND DISCUSSION

3.1. PREPARATION OF AgNPs/DA NANOCOMPOSITE

Firstly, diatomite was treated with 1% hydrochloric acid (v/v) in order to reduce mineral then washed and dried at 110°C before stirring with AgNO$_3$/chitosan solution. The aqueous ammonia was used as base to adjust the pH of suspension to 5-6. Reyad et al. (2003) and Caliskan et al
(2011) reported that the pHzpc (isoelectric point) of diatomite was ~ 4 so the diatomite surface may be negatively charged above pHzpc [19, 20]. The electrophilic silver ions (Ag\(^{+}\)) were adsorbed on the surface and embedded in amorphous silicon dioxide (SiO\(_2\)) with the nucleophilic oxide groups (SiO\(\cdot\)) by stirring formation of suspension before irradiation [21]. The solvated electrons (e\(_{\text{aq}}\)) with \(E^0(\text{H}_2\text{O}/e_{\text{aq}}) = -2.87\) V\(_{\text{NHE}}\) and \(\cdot\)H radicals with \(E^0(\text{H}^+/\cdot\text{H}) = -2.3\) V\(_{\text{NHE}}\) that were generated by water radiolysis can reduce adsorbed Ag\(^{+}\) ions to Ag atoms by irradiation effects in suspension solution (\(E^0(\text{Ag}^{+}/\text{Ag}) = -1.8\) V). Continuous reduction of the Ag\(^{+}\) ions causes the aggregation into AgNPs cluster (\(E^0(\text{Ag}^{+}_n/\text{Ag}_n) = 0.79\) V\(_{\text{NHE}}\)) [22]. Moreover, in chitosan solution, the radiolytic \(\cdot\)OH groups from irradiated water coordinate with chitosan by hydrogen abstraction to form macromolecule free radicals (R\(^{\cdot}\)). At a slight acid medium pH 5-6, hydronium ion H\(_3\)O\(^{+}\) represents an important scavenger for solvated electrons e\(_{\text{aq}}\) which are converted to \(\cdot\)H radicals (k = \(2.3 \times 10^7\) m\(^3\)mol\(^{-1}\)s\(^{-1}\)). These radicals also contribute to reduction of Ag\(^{+}\) in chitosan solution to Ag\(^0\), so the value of total reduction yield (\(G_{\text{red}}\)) is unchanged and close to maximal reduction yield (\(G_{\text{red,max}}\)) in theory [23]. In this study, the reaction mechanism for the reduction of adsorbed Ag\(^{+}\) on silica (SiO\(_2\)) in suspension of AgNO\(_3\)/chitosan/DA by electron irradiation can be proposed as follows:

\[
\begin{align*}
\text{Ag}^{+} + (\text{SiO}^-) & \rightarrow \text{Si-O}•••\text{Ag}^{+} \quad (1) \\
\text{H}_2\text{O} \quad (\text{EB}) & \rightarrow \cdot\text{OH} + e_{\text{aq}}^- + \cdot\text{H} + \text{H}_2\text{O}_2 + \text{H}_2 + \ldots \quad (2) \\
e^-_{\text{aq}} + \text{H}_2\text{O} & \rightarrow \cdot\text{H} + \text{H}_2\text{O} \quad k = 2.3 \times 10^7 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \quad (3) \\
\text{Si-O}•••\text{Ag}^{+} + e^-_{\text{aq}}(\cdot\text{H}) & \rightarrow \text{Si-O}•••\text{Ag}^{0} \quad (4) \\
\text{R(\text{chitosan})} + \cdot\text{OH}(\cdot\text{H}) & \rightarrow \text{R}^{\cdot}\text{H abstraction} + \text{H}_2\text{O}(\text{H}_2) \quad (5) \\
\text{Si-O}•••\text{Ag}^{+} + \text{R}^{\cdot}\text{H} & \rightarrow \text{Si-O}•••\text{Ag}^{0}\text{R}_1 \quad (6) \\
n\text{Si-O}•••\text{Ag}^{0}\text{R}_1 & \rightarrow \text{Si-O}•••\text{Ag}_2\text{R}_2 \rightarrow \text{Si-O}•••\text{Ag}_n\text{R}_n \quad (7)
\end{align*}
\]

The binding of silver clusters with chitosan as well as with silica surface of diatomite are achieved through the Ag–O–Si bonds. Besides, the protonated amine groups (R–NH\(_3^+\)) of chitosan in acidic medium can stabilize silver clusters by electrostatics repulsions [24].
FIG. 1 Effect of absorbed dose on the content of AgNPs in nanocomposite after removal of unbound silver on diatomite.

The absorbed dose plays an important role in formation and growth of AgNPs by EB-irradiation in situ synthesis in which Ag⁺ ions in AgNO₃/chitosan/DA suspension were reduced to Ag⁰ and simultaneously immobilized on diatomite. FIG. 1 clearly indicated that the content of AgNPs in nanocomposite gradually increased with dose from 6.5 to 20.2 kGy. Above 20.2 kGy (25.9 kGy), the AgNPs content coordinated with DA changed insignificantly and obtained an approximate efficiency about 0.13% from ICP-AES analysis. This data is similar to the results of EDX analysis for elemental components in AgNPs/DA nanocomposite (TABLE 1). An amount of unbound Ag onto DA was removed by washing samples after irradiation.
### TABLE 1 ELEMENTAL PERCENTAGES OF THE AgNPs/DA NANOCOMPOSITE

<table>
<thead>
<tr>
<th>Material</th>
<th>Element</th>
<th>O (%)</th>
<th>Na (%)</th>
<th>Al (%)</th>
<th>Si (%)</th>
<th>Ag (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>Weight%</td>
<td>57.63</td>
<td>1.76</td>
<td>1.63</td>
<td>38.98</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atomic%</td>
<td>70.25</td>
<td>1.49</td>
<td>1.18</td>
<td>27.08</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>AgNPs/diatomite</td>
<td>Weight%</td>
<td>57.70</td>
<td>1.64</td>
<td>1.93</td>
<td>38.60</td>
<td>0.13</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Atomic%</td>
<td>71.07</td>
<td>1.38</td>
<td>1.38</td>
<td>25.87</td>
<td>0.3</td>
<td>100</td>
</tr>
</tbody>
</table>

#### 3.2. PHYSICO-CHEMICAL CHARACTERIZATIONS OF AgNPs/DA NANOCOMPOSITE

The UV-vis spectra of the AgNPs colloidal solution in the AgNO$_3$/DA suspensions after EB-irradiation were shown in Fig. 2. The AgNPs colloidal solutions depicted peak maxima ($\lambda_{\text{max}}$) in the range from 417-422 nm respectively increase in absorbance with EB doses from 6.5 to 20.2 kGy. Above 20.2 kGy (25.9 kGy) the absorbance changed insignificantly. Therefore, the dose of 20.2 kGy was optimal for complete conversion of the 10 mM AgNO$_3$ to AgNPs in DA suspension with 1% chitosan solution at ambient temperature. Chitosan was not only stabilizer of AgNPs but also binder of AgNPs on diatomite through the intermolecular hydrogen bonds. According to previous studies on diatomaceous structure, the hydroxyl groups are primary reactive sites on the surface of diatomite [25, 26]. These functional groups can bind with hydroxyl (–OH) or amino (–NH$_2$) groups of chitosan which are able to form the intermediate connection between Ag$^0$ and DA.
FIG. 2 UV-Vis SPECTRA OF COLLOIDAL AgNPs FROM 10mM AgNO₃/DA SUSPENSION CORRESPONDING TO ABSORBED DOSES OF: (a) 6.5 kGy, (b) 13.4 kGy, (c) 20.2 kGy and (d) 25.9 kGy.

FIG. 3 shows SEM images of DA and AgNPs/DA samples. The image revealed the blank porous structure of DA in FIG. 3a. On the other hand, the morphology of AgNPs/DA indicated that the particles were loaded into pores of DA which could be attributed to the presence of silver nano (FIG. 3c). The elemental compositions of DA are determined by EDX spectrum in FIG. 3b including peaks of O, Na, Al and Si at 0.5, 1.1, 1.5 and 1.8 keV, respectively. The EDX spectrum of AgNPs/DA nanocomposite depicted a new peak of Ag at 3 keV besides similar elements to component of DA (FIG. 3d). Results in TABLE 1 also showed the weight and atomic percentages of Ag in AgNPs/DA nanocomposite in comparison with DA.

The shape and dispersion of AgNPs on the surface of DA are shown by TEM image of the AgNPs. This nanocomposite was prepared by EB irradiation of 10mM AgNO₃/diatomite in 1% chitosan solution at the dose of 20.2 kGy. The TEM image in FIG. 4a shows the AgNPs with spherical morphology that are well dispersed without aggregation on the surface of DA. In addition, a narrow size distribution of AgNPs/chitosan also indicated that AgNPs are homogeneous at experimental conditions (FIG. 4b). The size, shape and the formation rate of the metal nanoparticles which have been synthesized by irradiation depend on the irradiation dosage, the concentration of initial component and other conditions [27]. The presence of AgNPs in SiO₂ matrix demonstrated that the nanocomposite of AgNPs/DA can be synthesized by in situ reduction of AgNO₃ in DA suspension containing SiO₂ under EB irradiation. The average diameter of the
AgNPs prepared at the dose of 20.2 kGy was determined from TEM image to be 9.3 nm. The advantage of embedding AgNPs in DA matrix was dispersion of AgNPs through silica avoiding their aggregation, so small sized AgNPs with a typical diameter between 1-10 nm were formed [28].

FIG.3 SEM IMAGES AND EDX SPECTRA RESPECTIVELY FOR THE DIATOMITE (a, b) AND AgNPs/DA NANOCOMPOSITE (c, d) AT THE DOSE OF 20.2 kGy
3.3. ANTIBACTERIAL ACTIVITIES OF AgNPs/DA NANOCOMPOSITE

FIG. 4 TEM IMAGE (a) AND PARTICLE SIZE DISTRIBUTIONS (b) OF AgNPs AT THE DOSE OF 20.2 kGy

FIG. 5 PHOTOGRAPHS OF ANTIBACTERIAL TEST RESULTS AGAINST *E. coli* (10^3-10^6 CFU/ml): THE SURVIVAL OF *E. coli* ON LB (A); AgNPs/DA NANOCOMPOSITE (B); DA (C)
FIG. 5 shows the test results for antibacterial efficacy against *E. coli* of samples, namely the control, the blank DA and the AgNPs/DA nanocomposite with 0.13% of AgNPs in nanocomposite. The control specimens show the overgrowth of bacteria on the LB nutrient substrate in Fig. 5A, 5C1. The bacterial counts decreased after a contact time of 30 min with all samples containing DA which adsorbed bacteria into porous DA (Fig.5B, 5C). Especially, the nanocomposite of DA deposited AgNPs inhibited remarkably the growth of *E. coli* (Fig. 5B). The survival percentages of *E. coli* on LB agar for the specimens of AgNPs/DA in comparison with control were ~ 100 %.

According to Egger et al. (2009), the silica matrix structure acts a convenient carrier for incorporating with metal nanoparticles as AgNPs by dispersion of discrete silver nanoparticles throughout silica and limitation for release of AgNPs, resulting in long-term antibacterial efficacy [27]. In this study, nanocomposite containing AgNPs immobilized on DA was tested to determine its antibacterial activity against contaminative *Aeromonas hydrophila* bacteria for catfish (*Pangasianodon hypophthalmus*) in Vietnam. The experiment was carried by incubation with AgNPs/DA at various concentrations of AgNPs for 3h and 24h. The test results for *Aeromonas hydrophila* showed that antibacterial activity depends upon the content of AgNPs in composition. No bacteria survived on BHIA plates cultured bacteria which were incubated with AgNPs/DA containing 0.13% AgNPs at concentration of 26 μg/ml media for 3 and 24h (FIG. 6a, 6b). However, the colonies were overgrowth on the control samples with sterilized water (FIG. 6 control). FIG. 6c also showed negligible antibacterial activity at lower concentration of AgNPs (0.079%).
These small sized-AgNPs possess large surface areas, enabling them to have large contact areas with the bacterial cells, leading on the increase in permeability of cell membranes and disturbance of respiration. Moreover, the aerobic environments of the antibacterial tests allow for the partial surface oxidation of the AgNPs, resulting in generating Ag$^+$ ions that can disrupt ATP (adenosine triphosphate) production to inhibit the phosphate adsorption of bacterial protein. Dina et al. (2017) also demonstrated the prolonged antibacterial effects of silver nano-silica composite against methicillin-resistant Staphylococcus aureus (MRSA) and E. coli after 14h, 48h and even 72h [28]. According to these authors, their silver nanoparticles - silica composite is a promising candidate has been used as antibacterial, antifungal and antiviral agents.
4. CONCLUSIONS

The silver ions were reduced to atoms by EB irradiation and simultaneously deposited on the diatomite by in situ synthesis for preparation of AgNPs/DA nanocomposite. The dispersion of AgNPs in silica of diatomite avoiding their aggregation so that a diameter of AgNPs <10 nm was formed.

The AgNPs/DA nanocomposite exhibited good antibacterial activity against *E. coli* and *Aeromonas hydrophila*. The inhibition of microbial growth due to surface contact with the AgNPs/DA nanocomposite demonstrated that material functionalized AgNPs have excellent antimicrobial properties.

Testing antibacterial efficacy against other infectious bacteria for catfish (*Pangasianodon hypophthalmus*) in aquaculture will be carried out for further study.

REFERENCES

ANNEX II

TECHNOLOGICAL CHALLENGE BY DOMAIN OF APPLICATION (ALL CONTRIBUTION)

1. Environment

Environmental Protection, Control and Remediation can benefit from the recent advances in nanotechnologies and nanomaterials. The current limitations identified during the meeting relate to lack of sensitivity, robustness, integrability and cost-efficiency. Effective solutions for water purification, sensing and removal of pollutants need to be cost-effective, competitive and scalable. 

In this field of application, the main technological challenges to be addressed include:

- Need for production of stable and cost-efficient catalysts for removing of organic dyes from water sources.
- End-product must be competitive in terms of both performance and cost.
- Assurance that the obtained product works with existing SPR spectroscopy equipment.
- Assurance of the chemical and mechanical stability of hybrid materials in order to obtain a safely and efficient use of this materials in field consolidation of stone/based materials;
- Make the hybrids functionalization dependent uniquely from ionic liquid used and irradiation parameters for expedite and low-cost production
- Increment of applied ion beam current from an electron beam ion source (EBIS) in order to achieve the desired pore density in membrane filter production.
- Mass production of filters with uniform spread of SHI beams on polymers.
- Obtainment of titania-based conductive polymeric materials able to respond in visible light range.

2. Electronics and energy

In the electronics and energy fields, possible technological challenges are mainly classified in two issues—materials and interfaces, both of which are related to the control of their nanostructures through radiation processing. Through these challenges, two outputs will be expected. One is the
development of less expensive alternatives to the currently used materials. The other challenge is the development of new materials or methodology to access them, which has not yet been addressed so far. Durability and scalability are also the important factors for practical industrial applications.

In this field of application, the main technological challenge to be addressed are as follows:

- Development of assembling process to obtain nanoscale p-n heterojunctions from organic nanowires for photon-energy conversion devices
- Development of carbon based nanowires with sufficient electrical/thermal conductivities
- Metal NPs for soft nanoelectronics, Stimuli-responsive nanoelectronics Development of methodologies to control the morphology of noble metal nanoparticles.
- Improvement construction strategies of hydrogel nanoactuators to achieve bending motions for optical sensor applications.
- Development of concept of computational modeling to understanding activation mechanism of combined photothermal/bending kinetics for soft electronic application
- Quantification of defects through structural analysis and analysis of effects on ferromagnetic resonance
- Examination of applicability to electronic devices using magnetic thin films
- Proposal of technical model by matching experimental results with theory
- Design of practical nanostructure synthesis systems and definition of practical printing techniques ready to be used as conductive inks for the fabrication of RFID/NFC tags
- Design the synthesis techniques and protocols that can be simplified and scaled-up for industrial transfer
- Looking for less expensive raw materials to decrease the dependence on expensive raw materials: noble metallic nanoparticles for fuel cells/supercapitors/batteries
- Nanocomposites that exhibit performance comparable or higher than the current technology used in electrochemical energy devices.
- Developing scalable and commercially viable fabrication techniques for the electrochemical energy device
- Improve durability of the current electrochemical energy devices
- Increasing efficiency and lowering costs of component fabrication
• Using low-cost raw materials, reducing the amount of materials used, and reducing the cost of industrial processes of manufacturing
• Using thin films of Si to reduce cost and obtain compact systems for Si platelets formation for photovoltaics

3. Medicine, Healthcare, Cosmetics

In this vital field of application, the fabrication of nanomaterial-based products for medical treatment, healthcare products and cosmeceuticals must be developed and scaled guided by biocompatibility, non-toxicity and preferable use of natural materials.

In this field of application, the main technological challenge to be addressed are as follows:

• Need for production of stable and cost-efficient antimicrobial coatings for every-day applications (e.g., sportswear, etc.)
• Need for development of the methods for fabrication of new hydride-type nanocarriers to be used as selective radiosensitizers in cancer therapy
• Development of periodontal splints from natural polymers such as nanochitosan-microbial cellulose blending which has antibacterial and anti-inflammation prepared and sterilized by radiation
• Looking for ideal periodontal splint such as: easy to use and replace, economic, stable and efficient, non-irritating/no-toxic, not interfere with treatment, aesthetically acceptable, and not provoke iatrogenic diseases
• Preparation of nano-chitosan of appropriate size through ionic gel using TPP crosslinker
• Stabilization of nano-chitosan particle size
• Methods of blending of nano-chitosan/microbial cellulose in order to get an effective antimicrobial and anti-inflammation properties and high mechanical properties and possible to attach to the bond material for stabilization and immobilize the movement of teeth
• To control the bioactivity, porosity and surface morphology of hybrid materials in reproducible way for successful bone consolidation
• Consideration of bio-based materials and mild condition to develop nanomaterials for medical, healthcare, cosmeceutical purposes.

• Design of the appropriate nanostructure system and development of optimized protocol, techniques and manufacturing processes for synthesis of polymeric nanoparticles that can be simplified and scaled-up for industrial transfer in medical, healthcare, cosmeceutical applications.

• Consideration of health and safety issues of the developed nanomaterials for medical, healthcare, cosmeceutical purposes.

• Preparing manufacturing protocols of nanoparticle use in potential applications

4. Chemical industry, catalysis

In this field of application, it is important to develop new approach for fabrication of nanoparticle-based catalysts featuring high catalytic activity, high stability, reusability and cost-efficiency.

In this field of application, the main technological challenge to be addressed are as follows:

• Need for development of new cost-efficient hybrid-type film catalysts for synthetic chemistry

• Need for development of new cost-efficient composite porous catalysts for synthetic chemistry

• Increasing of catalytic activity of metal nanoparticles in terms of the stabilizing matrix through the establishment of a method yielding tailor-made and well-defined characteristics in order to finely tune the graft densities and architectures and to achieve reproducible synthesis pathways.

• Looking for less expensive nanocomposite with comparable or higher performance than Pt or Au, that have been used current to the reforming PROx-CO process.

• Powder nanocomposites

• Developing radiation chemical protocols for the synthesis of monodispersed and optimally sized carbon-supported noble metal NP catalysts with high activity and stability;

• Optimising catalytic properties of a metal-carbon nanocomposite by tuning its size, shape and composition to achieve the best possible performance;
• Promoting radiation processing technique for the mass production of supported metal NP

5. Materials

Within this application domain, multiple areas for development have been identified, including: composites, packaging, cultural heritage, coatings, materials with specific properties.

In these fields of application, the main technological challenges to be addressed are as follows:

• Need for development of new cost-efficient methods for production of soft hybrid metal-polymer materials with specific magnetic and optical properties (to be used for advanced applications in electronics and photonics)

• Need for development of new cost-efficient and environmentally friendly methods for production of porous composites with embedded metallic nanotubes

• To find out what type of starting organic molecules afford orthogonal orientation to the substrate for superhydrophobic surfaces modified with nanowires

• To survey whether the orthogonal nanowires are tolerant (sufficient mechanical strength) to water droplet; if not, to achieve higher mechanical strength by increasing the number density of nanowires with increased fluence of irradiation

• Identification of suitable, and possibly scalable, manufacturing technologies for the development of (nano) composites polymeric material which, in the case of active materials, are able to maintain the effectiveness of active compounds after processing.

• Removal of the catalysts form the reaction mixture by a facile way (e.g. magnetic properties) in heterogeneous (solid) catalysts in the transesterification process

• The fine tune of the characteristics of the modifications carried out

• Achievement of promising methods for reproducible properties in applications

• Maintenance of the hybrid materials nanostructure with the introduction of ionic liquids in their composition is essential for successful commercial applications;

• To prepare functionalized hybrid materials by radiation processing in an expeditious and affordable way;
• Adequate pairs and ratios of precursors/ionic liquids for an easy and affordable production of functionalized hybrid materials;
• To improve and enlarge the range of biocide activity of hybrid materials;
• Challenges for continuous graphene as excellent corrosion barrier continue to overcome.
• Graphene applicability cannot be effectively realized unless facile techniques to synthesize high quality, large area graphene are developed in a cost-effective way. Ionizing radiation can be used to obtain graphene in a large scale and relative low cost.
• The weak adhesion of graphene on metals influences its practical use in anticorrosive coatings, especially at long-term. Also, it is difficult to apply graphene onto rough surfaces, both of which significantly limit the universal use of graphene on substrates in practical use exposure to corrosive environments. To address these problems, graphene/nano-composite prepared by radiation could be used to solve these issues.
• Design of appropriate nanostructure synthesis system and development of optimized coating/printing techniques that can be simplified and scaled-up for industrial transfer in coating and printing applications.
• Developing and optimizing techniques and procedures for synthesis of polymeric nanoparticles of desired structural parameters.
• Preparing manufacturing protocols of nanoparticle use in potential applications

6. Food and agriculture

In this field of application, it is important to develop new approach for fabrication of nano-fertilizers or nano-encapsulated nutrients that can be applied for minimizing nutrient, minimizing the loss of fertilizer and increasing crop yield. Another important goal is to produce active nanoparticles and nanocomposite films for shelf life extention of packaged food products.

In this field of application, the main technological challenge to be addressed are as follows:

• Considering the bio-based materials and green technology to develop nanomaterials for plant growth, crop production, extending food self-life.
• Design of the appropriate nanostructure synthesis system and development of optimized protocol, techniques and manufacturing process for of nanoparticles and polymeric films
that can be simplified and scaled-up for industrial transfer in food, agricultural and aquaculture applications.

- Optimizing quality, amount, cost, side effects of nanomaterials used for food and agriculture.
- Concerning the environmental effect of nanomaterials in soil and irrigation system and the safety issues related to cytotoxicity and eventual migration of radiolytic products from irradiated (nano)composite polymeric films
- Maintenance of the hybrid materials nanostructure with the introduction of ionic liquids in their composition;
- Adequate pairs and ratios of precursors/ionic liquids;
- Make the hybrids functionalization dependent uniquely from ionic liquid used and irradiation
## ANNEX III

<p>| Country       | UV-Vis | IR   | Raman | Elemental | HPLC | GC   | GC-MS | GC-MS-MS | GC-MS-MS-MS | DSC | DTA | TGA | TMA | DMA | XRD | XRF | AFM | FEM | EDX | -SEM | XPS | STM | -TEM | NMR | SLS | DLS | PARTICLE | SLS | -WAXD | POROSITY | WATER | DRY | WATER | FREEZE | NETWORK | NEUTRON | ACT | PULSE | DC | MICROWAVE | ECR | 3D PRINTER | ESR/EPR | VIDEOR | STIRRER |
|---------------|--------|------|-------|----------|-------|------|-------|----------|------------|------|------|-----|-----|-----|------|------|------|-----|-----|-----|------|------|-------|------|------|------------|-------|------|-------|--------|----------|---------|----|------|---|-------------|-----|------------|------|-------|---------|
| Brazil        |        |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Egypt         | X X X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| France        | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Indonesia     | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Italy         | X X X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Japan         | X X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Kazakhstan    |        |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Korea (Kim)   | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Korea (Lee)   |        |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Malaysia      | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Morocco       | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Philippines   | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Poland        | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Portugal      | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Russia        | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Serbia        | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Thailand      | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |
| Turkey        | X X |      |       |          |       |      |       |          |             |      |      |     |     |     |      |      |      |     |     |     |      |      |        |      |      |            |      |      |        |        |          |         |    |      |   |             |     |            |      |       |          |</p>
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ANNEX IV

The First Research Coordination Meeting on 'Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology'
18-22 March 2019, Vienna IAEA HQ (C0234)

MEETING AGENDA

Monday, 18 March 2019

08:00 - 09:00  Registration at the Gate 1, IAEA headquarters, VIC

Session I:  Introductory Session

09.00 - 09.30  Opening of the meeting by:
- Ms Melissa Denecke, Director NAPC (IAEA)
- Mr Joao Alberto Osso Junior, Section Head of RPRT (IAEA)
- Mr Bumsoo Han, Scientific Secretary, RPRT (IAEA)
- Ms Valeriia Starovoitova, RPRT (IAEA)
- Ms Dinara Abbasova, RPRT (IAEA)

Scope and Objectives of the Meeting, Adoption of the agenda
Election of the chairperson of the meeting, introduction of participant

<table>
<thead>
<tr>
<th>Session II:</th>
<th>Participants’ Presentations</th>
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</thead>
</table>
| 09:30 – 10:10 | Ms Solange Kazumi Sakata  
(Brazil)  
Sustainable Synthesis of Metal, Metal Oxide/Graphene Based Nanocomposites for Renewable Energy Sources and Storage |
| 10:10 – 10:30 | Coffee Break |
| 10:30 – 11:10 | Mr Hassan Ahmed Abd El-Rehim  
(Egypt)  
Radiation Synthesis of Graphene Composites and Their Use as Anti-corrosion Materials |
| 11:10 – 11:50 | Mr Xavier Coqueret  
(France)  
Radiation-induced elaboration of nanocomposites in dimensionally controlled macro- or microstructures |
| 11:50 – 12:30 | Mr Darmawan Darvis  
(Indonesia)  
Synthesis of Nano Chitosan-Cellulose Microbial (CH-CM) Composite for Splint Teeth in Periodontal Application |
| 12:30 – 14:00 | Lunch Break |
| 14:00 – 14:40 | Ms Giovanna Giuliana Buonocore  
(Italy)  
Application of nanotechnology and radiation processing in the development of advanced materials for food packaging sector |
Mr Tsuneaki Sakurai (Japan)  
Development of organic nanowires via polymerization in single ion tracks triggered by high energy particle irradiation

15:20 – 15:40  
Ms Anastassiya Mashentseva (Kazakhstan)  
Radiation Induced and Template Synthesis of the Photo-catalytically Active Ion-Track Membrane Composites

15:40 – 16:20  
Mr Hyun Bin Kim (Republic of Korea)  
Nanomaterial Fabrication using radiation technology and its applications for electronic devices

Ms SeungHyun Lee (Republic of Korea)  
Development of Core Technologies of Swift Heavy Iron Beams for Track-Etched Membrane

18:00 – 20:00  
Welcome Drinks (sponsored by the IAEA)

Tuesday, 19 March 2019  
Session III: Participants’ Presentations

Ms Kuan Ying Kok (Malaysia)  
Radiation Processing of Electro catalysts for the Enhancement of Catalytic Performance in Renewable Energy Devices

Mr Hicham labrim (Morocco)  
Exploitation of the Radiation Induced Effects for Thin Film Production
10:20 – 10:40

**Coffee Break**

10:40 – 11:20

Mr Jordan Madrid
(Philippines)

Radiation-Induced Synthesis of Nanostructured Materials for Analytical Application

11:20 – 12:00

Mr Piotr Ulański
(Poland)

Radiation Synthesis of Polymer - and Metal - Based Nanomaterials - New Methods and Products

12:00 – 12:40

Mr Luis Ferreira
(Portugal)

Nanostructured Hybrid Materials by Radiation Processing Assisted by Ionic Liquids

12:30 – 14:00

**Lunch Break**

14:00 – 14:40

Mr Vladimir Feldman
(Russia)

Development of new approach to fabrication and modification of nanostructures and nanohybrid materials using X ray irradiation

14:40 – 15:20

Ms Jelena Krstic
(Serbia)

Development of Hydrogel Nanoactuators Based on Gold Nanoparticles, Poly (N-Isopropylacrylamide) and Poly (Vinyl Alcohol) Using Radiation Technology for Soft Electronics

15:20 – 16:00

Ms Wanvimol Pasanphan
(Thailand)

Radiation-controlled diversity of nanostructures for industrial applications: coatings/printings, cosmeceuticals and agrochemicals

16:00 – 16:20

**Coffee Break**
16:20 – 17:00
Mr Murat Barsbay (Turkey)
Formation of palladium nanoclusters via radiation-induced reduction of Palladium ions absorbed on poly (vinylpyrrolidone) shell grafted on silica microparticles by RAFT polymerization and investigation of their catalytic activities

17:00 – 17:40
Mr Aliaksandr Baidak (UK)
Investigation into radiation chemical synthesis of noble metal nanoparticles on carbon supports for applications in electrocatalysis

17:40 – 18:20
Ms Thi Hanh Trunong (VietNam)
Preparation of Silver Nano/Diatomite Nanocomposite by Irradiation Method in Order to Treat the Pathogenous Bacteria for catfish (Pangasianodon hypophthalmus).

Wednesday, 20 March 2019

Session V & VI:
Discussion on the Directions for Research and Development
(ALL PARTICIPANTS)

09:00 – 10:30
Discussion and Identification of Emerging Needs and Gap Areas in the Research and Development for Nano-products

10:30 – 11:00
Coffee Break

11:00 – 12:30
Discussion and Identification of Emerging Needs and Gap Areas in the Research and Development for Nano-products
12:30 – 14:00  
*Lunch Break*

14:00 – 15:00  
Discussion on Directions for Research and Development

Ms Nicola Gulley  
Section Head of Publishing Sec.  
*Guidelines and Format of the IAEA publication (IAEA)*

15:30 – 16:00  
*Coffee Break*

16:00 – 17:30  
Discussion for Cooperative and Networking Activities among the Participating Laboratories

17:30 – 18:00  
*Finalize and document the discussion*

**Thursday, 21 March 2019**

Session VII:  
**Finalizing Participants’ Work Plan and Preparation of Technical Document (ALL PARTICIPANTS)**

09:00 – 10:30  
Adjustment of Participants’ Work Plans Based on the Discussions
<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>10:30 – 11:00</td>
<td>Coffee Break</td>
</tr>
<tr>
<td>11:00 – 12:30</td>
<td>Finalizing Participants’ Work Plans</td>
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<tr>
<td>12:30 – 14:00</td>
<td>Lunch Break</td>
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<tr>
<td>14:00 – 15:30</td>
<td>Preparation of the Meeting report: scope/contents/structure of the meeting report/conclusions/recommendations</td>
</tr>
<tr>
<td>15:30 – 16:00</td>
<td>Coffee Break</td>
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<tr>
<td>16:00 – 17:30</td>
<td>Drafting of the Meeting Report</td>
</tr>
<tr>
<td>17:30 – 18:00</td>
<td>Finalize and document the discussion</td>
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</table>

**Friday, 22 March 2019**

**Session VIII:** Final Review and Acceptance of Meeting Report
09:00 – 10:30  Review of the Draft Meeting Report

10:30 – 11:00  Coffee Break

11:00 – 12:30 Finalizing and Acceptance of the Meeting Report

12:40 – 14:00 Lunch Break

14:00 – Closing of the Meeting
ANNEX V

F22070-CR-1
First Research Coordination Meeting on Enhancing the Beneficial Effects of Radiation Processing in Nanotechnology
Vienna, Austria
18 March 2019 - 22 March 2019

List of Participants
(as of 2019-03-21)

<table>
<thead>
<tr>
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<th>Authority</th>
<th>Personal Details</th>
</tr>
</thead>
</table>
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| 21    | United Kingdom | Mr Aliaksandr BAIĐAK  
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| 25 | IAEA | Ms Valeria STAROVOITOVA  
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